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THE OBJECTIVE OF THIS STUDY WAS THE IDENTIFICATION OF TECHNOLOGIES FOR RESEARCH AND DEVELOPMENT THAT PROMISED REASONABLY COST-EFFECTIVE ENGINEERING SOLUTIONS FOR THE ARMY'S SOIL CONTAMINATION PROBLEMS.

57 TECHNOLOGIES WERE ASSESSED FOR 1) FEASIBILITY, 2) AVAILABILITY THROUGH COMMERCIAL SOURCES, AND 3) MERIT FOR INVESTING CAPITAL IN FURTHER RESEARCH AND DEVELOPMENT.

INFORMATION ABOUT EACH TECHNOLOGY INCLUDES:

- 1. BRIEF DESCRIPTION
- 2. APPLICABILITY
- 3. COMMENTS
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INSTALLATION RESTORATION GENERAL ENVIRONMENTAL TECHNOLOGY DEVELOPMENT

Final Report

Removal of Contaminants from Soil

Phase I: Identification and Evaluation of Technologies

Lawrence J. Bove Cheryl L. Cundall Walter P. Lambert, Ph.D. Peter J. Marks Joseph F. Martino

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December 1983

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•			Page
Paragraph	1 IN	TRODUCTION	1
J	1.1	General	. 1
	1.2	Background	1
	1.3	Objective and goal	1
	1.4	Approach to technology assessment	2
	1.5	Concepts and definitions	4
		REATMENT/PERFORMANCE CRITERIA	5
	2.1	Regulatory environment for soil contam-	
	2.1	ination	5
	3 TE	ECHNOLOGY IDENTIFICATION AND CHARACTERI-	
	J 11	ZATION	9
	3.1	Selection of technologies	9
	3.2	Thermal processes	14
	3.2.1	Vertical well chemical reactor	14
	3.2.1.1	Description	14
	3.2.1.2	Applicability	14
	3.2.1.2	Comments	17
	3.2.1.3	References	17
-		Multiple hearth incinerator	18
	3.2.2	Description	18
	3.2.2.1	Applicability	18
	3.2.2.2	Comments	20
	3.2.2.3		20
	3.2.2.4	References	21
	3.2.3	Incineration with a rotary kith	21
	3.2.3.1	Description	21
	3.2.3.2	Applicability	21
	3.2.3.3	Comments	24
	3.2.3.4	References	25
	3.2.4	Molten salt incinerator	25
	3.2.4.1	Description	25
	3.2.4.2	Applicability	26
	3.2.4.3	Comments	26
	3.2.4.4	References	29
	3.2.5	Fluidized bed incinerator	29
	3.2.5.1	Description	
	3.2.5.2	Applicability	29
	3.2.5.3	Comments	29
	3.2.5.4	References	29
	3.2.6	Wet air oxidation (WAO)	31
	3.2.6.1	Description	31
	3.2.6.2	Applicability	31



		Page
3.2.6.3	Comments	33
3.2.6.4	References	33
3.2.7	In-situ vitrification	34
3.2.7.1	Description	34
3.2.7.2	Description	34
3.2.7.3	Comments	34
3.2.7.4	References	. 36
3.2.8	Plasma torch	37
3.2.8.1	Description	37
3.2.8.2	Applicability	37
3.2.8.3	Comments	40
3.2.8.4	References	40
3.2.9	References	41
3.2.9.1	Description	41
3.2.9.2	Applicability	41
3.2.9.3	Comments	
3.2.9.4	References	
3.2.10	Burning/torching	42
	Description	42
3.2.10.2	Applicability	42
3.2.10.3	Comments	42
3.2.10.4	References	42
3.2.11		43
3.2.11.1	Description	43
3.2.11.2	Applicability	43
3.2.11.3	Comments	43
	References	
3.2.12	In-situ hot air or steam stripping	45
3.2.12.1	Description	45
	Applicability	
3.2.12.3	Comments	45
3.2.12.4	References	45
3.2.13		47
3.2.13.1	Description	47
3.2.13.2	Applicability	47
	Comments	48
	References	48
	Laser-initiated thermal decomposition .	50
	Description	50
	Applicability	50
	Comments	50
	Peferences	51



		Page
3.2.15	Supercritical water oxidation	52
3.2.15.1	Description	52
3.2.15.2	Applicability	52
3.2.15.3	Comments	52
	References	54
3.2.16	High-temperature fluid wall (HTFW)	55
	Description	55
	Applicability	55
	Comments	55
3.2.16.4	References	56
3.3	Chemical processes	59
3.3.1	Sulfur-based reduction (sulfide precip-	
	itation)	59
3.3.1.1	Description	59
3.3.1.2	Applicability	59
3.3.1.3	Comments	61
3.3.1.4	References	61
3.3.2	Chemical reduction with sodium borohy-	
	dride (NaBH ₄)	62
3.3.2.1	Description	62
3.3.2.2	Applicability	62
3.3.2.3	Comments	62
3.3.2.4	References	63
3.3.3	Solvent extraction (on-site)	65
3.3.3.1	Description	65
3.3.3.2	Applicability	65
3.3.3.3	Comments	65
3.3.3.4	References	66
3.3.4	Solvent extraction using the Acurex	
	process	69
3.3.4.1	Description	69
3.3.4.2	Applicability	69
3.3.4.3	Comments	69
3.3.4.4	References	69
3.3.5	Solvent extraction (in-situ)	71
3.3.5.1	Description	71
3.3.5.2	Applicability	71
3.3.5.3	Comments	71
3.3.5.4	References	71
3.3.6	Decontamination of soils using Franklin	
	solvent	74
2 2 6 1	Description	74



		Page
3.3.6.2	Applicability	74
3.3.6.3	Comments	74
3.3.6.4	References	74
3.3.7	Free radical oxidation	75
3.3.7.1	Description	75
3.3.7.2	UV/ozone	75
3.3.7.3	Gamma irradiation	77
3.3.7.4	Electron beam	78
3.3.7.5	Ultrasonic treatment	78
3.3.7.6	References	79
3.3.8	Free radical oxidation (Enercol oxida-	
	tion process)	80
3.3.8.1	Description	80
3.3.8.2	Applicability	80
3.3.8.3	Comments	80
3.3.8.4	References	81
3.3.9	Fenton's reagent	83
3.3.9.1	Description	83
3.3.9.2	Applicability	83
3.3.9.3	Comments	83
3.3.9.4	References	83
3.3.10	Base-initiated decomposition (alkaline	
	hydrolysis)	85
	Description	85
3.3.10.2		85
3.3.10.3		85
	References	85
3.3.11	Carbon adsorption	88
3.3.11.1	Description	88
3.3.11.2	Applicability	88
3.3.11.3	Comments	90
3.3.11.4	References	90
3.3.12	Ion exchange	91
3.3.12.1	Description	91
	Applicability	91
	Comments	91
	References	92
	Surfactant complexing	94
	Description	94
	Applicability	94
	Comments	95 05
7.7.17.4	References	95



		Page
3.3.14	Removal of metals and complexes with	
3.3.1	dithiocarbamate	96
3 3 14 1	Description	96
3.3.14.2	Applicability	96
3 3 14 3	Comments	96
	References	96
3.3.15	Philadelphia Quartz (PQ) process for	70
3.3.13	removing heavy metals	98
2 2 1 5 1		98
	Description	98
3.3.13.4	Applicability	98
3.3.15.3	Comments	
	References	98
3.3.16	Removal of heavy metals using cellulose	100
	xanthate	100
	Description	100
3.3.16.2	Applicability	100
3.3.16.3	Comments	100
· ·	References	100
3.4	Biological processes	102
3.4.1	Microbial bioaccumulation of metals	102
3.4.1.1	Description	102
3.4.1.2	Applicability	102
3.4.1.3	Comments	102
3.4.1.4	References	103
3.4.2	Immobilized cells	104
3.4.2.1	Description	104
3.4.2.2	Applicability	104
3.4.2.3	Comments	104
3.4.2.4	References	104
3.4.3	Vermicomposting	105
3.4.3.1	Description	105
3.4.3.2	Applicability	105
3.4.3.3	Comments	105
3.4.3.4	References	106
3.4.4	Composting	107
3.4.4.1	Description	107
3.4.4.2	Applicability	107
3.4.4.3	Comments	107
3.4.4.4	References	108
3.4.5	Aerobic biodegradation	110
3.4.5.1	Description	110
	Applicability	110



		Page
3.4.5.3	Comments	110
3.4.5.4	References	111
3.4.6	Aerobic biodegradation activated	
	sludge	112
3.4.6.1	Description	112
3.4.6.2	Applicability	112
3.4.6.3	Comments	112
3.4.7	Aerobic biodegradation rotating bio-	
	logical contactor (RBC)	114
3.4.7.1	Description	114
3.4.7.2	Applicability	114
3.4.7.3	Comments	114
3.4.8	Aerobic biodegradation bioponds	116
3.4.8.1		116
3.4.8.2	Description	116
3.4.8.3	Comments	116
3.4.9	Fluidized bed biological treatment	117
3.4.9.1	Description	117
3.4.9.2	Applicability	117
3.4.9.3	Comments	117
3.4.9.4	References	117
3.4.10	Landfarming	118
3.4.10.1	Description	118
3.4.10.2		118
3.4.10.3	Comments	118
3.4.10.4		118
3.4.11	Anaerobic biodegradation	120
3.4.11.1		120
3.4.11.2	Applicability	120
3.4.11.3	Comments	120
	References	120
3.4.12	Anaerobic/aerobic cycling	123
3.4.12.1	Description	123
3.4.12.2	Applicability	123
3.4.12.3	Comments	123
3.4.12.4	References	123
3.4.13	Biodegradation use of adapted micro-	
	bial cultures	124
	Description	124
3.4.13.2	Applicability	124
	Comments	124
		125



			Page
3.4.14.3		•	126 126 126 126 127
3.4.15.1 3.4.15.2 3.4.15.3 3.4.15.4 3.5 3.5.1	decontamination system (GDS) Description		128 128 128 128 129 132
3.5.1.1 3.5.1.2 3.5.1.3 3.5.1.4 3.5.2 3.5.2.1 3.5.2.2 3.5.2.3	Description		132 132 134 135 135 135
3.5.2.4 3.5.3 3.5.3.1 3.5.3.2 3.5.3.3 3.5.3.4	References		136 138 138 138 139 139
3.5.4 3.5.4.1 3.5.4.2 3.5.4.3 3.5.4.4 3.5.5 3.5.5.1	Geological isolation	•	141 141 141 141 142 142
3.5.6.1 3.5.6.2 3.5.6.3 3.5.6.4 3.5.7 3.5.7.1	Microencapsulation	• •	144 144 144 145 146
3.5.7.2	Applicability		146



		Page
3.5.7.3	Comments	150
3.5.7.4	References	150
3.5.8	Macroencapsulation ("jacketing")	151
3.5.8.1	Description	151
3.5.8.2	Applicability	151
3.5.8.3	Comments	151
3.5.8.4	References	
3.5.9	High gradient magnetic separation	
	(HGMS)	153
3.5.9.1	Description	153
3.5.9.2	Applicability	153
3.5.9.3	Applicability	153
3.5.9.4	References	154
	Washout	156
3.5.10.1	Washout	156
3.5.10.2	Applicability	
3.5.10.3	Comments	157
3.5.10.4	References	157
Δ Τ'	References	±3 /
•	DEVELOPMENT	159
4.1	The assessment process	159
4.2	First-level assessment criteria	
4.2.1	Purpose of first-level assessment	161
4.2.2	First-level assessment criteria	163
4.2.2.1	Technology performance	163
4.2.2.2	Versatility	163
4.2.2.3	Incremental residual volume	163
4.2.2.4	Additional treatment requirements	163
4.2.2.5	Intermedia transport	163
4.2.2.6	Safety	163
4.2.2.7	Area or volume limitations	164
4.2.2.8	Future land use	
4.2.2.9	Contaminant interferences	164
4.2.2.10		
4.2.3	First-level assessment procedure	
4.2.4	Analysis of first-level assessment	169
4.2.4.1	Thermal processes	169
4.2.4.2	Chemical processes	170
4.2.4.3	Biological processes	171
4.2.4.4	Physical processes	171
4.2.5	Criteria for advancement to the second	· -
	level	772



			Page
	4.3.2.8 4.3.3 4.3.4 5 E	Second-level assessment criteria Time to commercialization Proprietary status Estimated relative commercialization cost Estimated relative operational costs Environmental impact Unit process interactions Versatility Questions for consideration Second-level assessment process Analysis of second-level assessment DISCUSSION, FINDINGS, AND RECOMMENDATIONS Discussion Findings	174 174 174 174 174 176 176 176 176 176 176 177 187 187
		Recommendations	191 193
			Dogo
	·		Page
APPENDIX		PHYSICAL PROPERTIES	A-1 B-1



FIGURES

			<u>Page</u>
FIGURE	1.	Work flow diagram for identification, assessment, and selection of tech-nologies (unit processes) showing the highest potential for topics for	
		research and development for removal or decomposition of contaminants of	
		interest in soil	3
	2.	Typical vertical well chemical reactor profile	15
	3.	Typical vertical well chemical reactor cross section	16
	4.	Typical multiple hearth incinerator	
	_	system (without afterburner)	19
	5.	Typical rotary kiln incinerator system.	22
	6.	Mobile rotary kiln incinerator	23
	7.	Process flow diagram molten salt in- cineration	27
	8.	Schematic diagram molten salt incin-	 ,
		erator	28
	9.	Typical fluidized bed incinerator system	30
	10.	Wet air oxidation process flow dia-	
•	. 7 7	gram	32
	11.	Proposed full-size vitrification unit .	35
	12.	Plasma arc reactor schematic	38
	13.	Cross-section of a plasma arc furnace .	39
	14.	Typical in-situ hot air/steam stripper.	46
	15.	Soil decontamination using microwave heating process flow diagram	49
	16.	Supercritical water oxidation proc- ess flow diagram	53
•	17.	Profile of a high-temperature fluid	
		wall reactor	57
	18.	Cross section of a high temperature fluid wall reactor	58
	19.	Sulfur-based reduction	60
	20.		00
		Sodium borohydride reduction process flow diagram	64
	21.	Typical on-site solvent extraction	
	-	process for soils	67
	22.	Nickel recovery from sulfide ores	68
	23.	Acurex process process flow diagram.	70
	24.	Typical site cleanup equipment	71



FIGURES

		Page
25.	In-situ solvent extraction process	
	schematic	73
26.	Mechanism for free radical oxidation .	76
27.	Enercol oxidation process process	
	flow diagram	82
28.	Fenton's reagent	84
29.	Base-initiated decomposition	86
30.	Reactions for base-initiated decomposi-	
	tion of explosives	87
31.	Carbon adsorption	89
32.	Ion exchange	93
33.	Metals removal using DTC process	07
	flow sheet	97
34.	PQ process for heavy metals removal	0.0
	process flow diagram	99
35.	Flow sheet of cellulose xanthate proc-	101
	ess for heavy metals removal	101
36.	Composting	109
37。	Aerobic biodegradation activated	113
	sludge treatment	115
38.	Rotating biological contactor	122
39.	Anaerobic digestion	130
40.	Actual GDS system in operation	131
41.	Typical secure landfill	133
42. 43.	Typical application of a slurry wall	137
44.	Cross-section of grouted bottom seal	20,
44.	beneath a containment area	140
45.	Cement-based stabilization process	148
46.	Lime-based (pozzolanic) stabilization	
40.	process	149
47.	Schematic representation of high gradi-	
1,,	ent magnetic separation for liquid	
	streams	155
48.	Typical washout system for demilitari-	
	zation of conventional munitions	158
49.	Work flow diagram for identification, .	
	assessment, and selection of tech-	
	nologies (unit processes) showing	
	the highest potential for topics for	
	research and development for removal	
	or decomposition of contaminants of	
	interest in soil	160



FIGURES

		Page
50.	Second-level technology evaluation pro-	
	cedure	175
51.	Summary of second-level assessment	178
52.	Development time frame within which	
	technology evaluations were made	180
53.	Categorization process for identifying	
	limited R&D targets	183
54.	Categorization process for identifying	
	unlimited R&D targets	185
55.	Technologies and types of experimental	
	studies recommended for further con-	
	sideration for the removal of con-	
	taminants from soil	190



TABLES

	Page
1. Summary of state regulations relat to soil contamination	6
2. Summary of criteria relative to so contamination	
	• • •
3. Thermal processes	
4. Chemical processes	12
6. Physical processes	
 Applicability of fixation for spec 	ific
contaminants	143
8. First-level assessment criteria fo evaluation of technologies poten ly applicable to removal or decosition of soil contaminants repo	tial- mpo- rted
for selected DARCOM installation	s 162
9. First-level evaluation summary res thermal technologies	ults:
10. First-level evaluation summary res	
chemical technologies	
11. First-level evaluation summary res	
biological technologies	
12. First-level evaluation summary res	
physical technologies	
physical technologies	
13. Technologies judged to be conceptu	arry
feasible for removal or decompos	173
of soil contaminants of interest	
Tat DCCOMM TOLCE CLUETURE CETACLE	177
<pre>15. Preliminary results of second-leve</pre>	182



1. INTRODUCTION

1.1 General. This report addresses the general topic of soil decontamination. Specific subjects to be addressed involve engineering methods for removal or decomposition of specific categories of soil contaminants.

This section of the report positions WESTON's work within the context of the continuing efforts by the Department of the Army to make their installations environmentally safe from unacceptable levels of toxic and hazardous substances. Recommendations are included for near-term process development topics that have the potential for use in future Army remedial action projects.

1.2 <u>Background</u>. Over recent decades, parcels of Army real estate have become chemically contaminated. Explosives, solvents, and heavy metals were released to the soil as wastes associated with Army industrial operations. Activities that contributed to soil contamination included equipment rebuilding and repair, munitions manufacturing, and munitions disposal.

In the early 1970's, the Installation Restoration Program was established. One of its objectives was to solve the problem of soil that was contaminated to unacceptable levels that limited the use of the land by the Army. In addition, pollution of off-post soil and groundwater has occurred, as well as contamination of off-post drinking water.

During the course of the program, it became evident that many of the chemical contaminants at Army installations are either unique to or predominantly associated with the military. Acceptable limits for these soil contaminants often have not been established and have had to be determined on a site-specific basis through negotiation between the Army and appropriate regulatory agencies. Very few processes for removal, decomposition, or immobilization of the soil contaminants were available, and were not necessarily applicable to the Army's specific problems.

1.3 Objective and goal. The primary objective of the work described in this report was the identification of technologies for research and development that promised reasonably cost-effective engineering solutions for the Army's soil contamination problems.

Specific goals of this study included the following:

(a) Provide problem classification/categorization.



- (b) Establish treatment/performance criteria (Section 2).
- (c) Identify state-of-the-art adaptable treatment concepts (Section 3).
- (d) Evaluate and rank order treatment concepts (Section 4).
- (e) Make recommendations for bench experimentation or field demonstration (Section 5).
- 1.4 Approach to technology assessment. This project was executed within the structured work flow pattern diagrammed on Figure 1. Work began with the identification of specific contaminants reported to be present in the soil of selected Army installations. Since removal or decomposition technologies may be affected by the combination of contaminants present, further analysis was made of how the reported contaminants occurred in combination with one another. After identification, the physical, chemical, biological, and environmental fate characteristics of the most important or most frequently-occurring contaminants were collected. This definition of what is present, in what combinations, and with what characteristics led to the identification of unit processes that could conceivably be applied toward removal or decomposition.

The question of feasibility was addressed next. Each of the identified technologies was researched through open and unpublished literature. Each technology was characterized by a list of preselected parameters. At the same time, a set of criteria was developed that defined feasibility to the applications of interest. Those criteria were used with the detailed technology descriptions to select the subset of conceptually feasible technologies from the set of conceptually applicable technologies. This was called the first level assessment.

Of the technologies that were conceptually feasible for removal or decomposition of the contaminants of interest, some were known to be available without further R&D work, some required further development, and some required so much further development that they were not practical targets within the context of the current Installation Restoration R&D program. Criteria were developed that defined this situation, and each of the conceptually-feasible technologies was evaluated against them. The result was a set of three lists, as follows:

(a) Technologies currently available that were feasible for the removal or decomposition of the contaminants of interest without the need for further development. These technologies might require site-specific evaluations but not further generalized R&D.

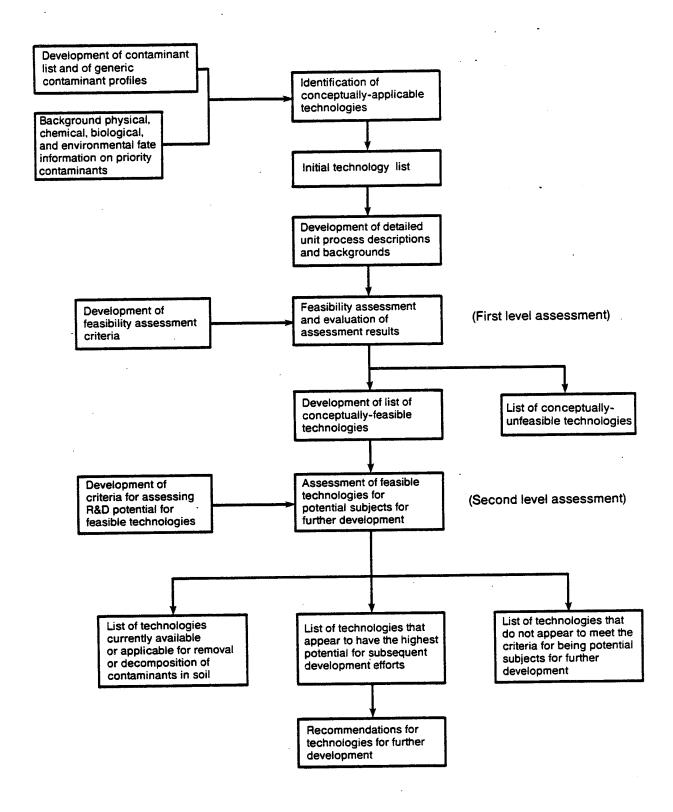


Figure 1. Work flow diagram for identification, assessment, and selection of technologies (unit processes) showing the highest potential for topics for research and development for removal or decomposition of contaminants of interest in soil.



- (b) Technologies that appeared to have a high potential for successful R&D within the bounds of the Installation Restoration Program. These technologies require further experimental or demonstration work, but appeared to be usable on a full-scale basis by 1987.
- (c) Technologies which, for a number of reasons, did not appear to be acceptable R&D topics.

This was called the second level assessment.

The product of the two assessments was a list of technologies that were recommended for further experimental or demonstration work.

- 1.5 Concepts and definitions. This project was executed within the bounds described by the operative concepts and definitions listed below.
 - (a) Removal. The generalized concept for removal of a contaminant from soil centered on the removal of that contaminant from access to the general environment. Therefore, processes that fixed a contaminant in a vitrified, nonleachable matrix, and processes that physically removed a contaminant from its original soil matrix to another location were both considered technologies that removed contaminants.
 - (b) Control volume. The soil matrix of interest in this study was bounded by the soil surface, the bottom of saturated sediments, and the top of the saturated zone. Sediments were the subject of other research efforts and were excluded from this study. The saturated zone and its associated groundwater were also subjects of other studies and were not considered.
 - (c) Soil technologies. Unit processes considered in this study were those that dealt directly with contaminated soils. A parallel effort under this same contract addressed the treatment of groundwater. Technologies identified under that project would have applicability in the treatment of aqueous extracts of contaminated soils, but those technologies were not within the scope of this study.



2. TREATMENT/PERFORMANCE CRITERIA

2.1 Regulatory environment for soil contamination. Current state and Federal regulations relating to soil contamination are in the developmental stages. Presently, there are only limited standards on Federal and state levels that can be applied to contamination of soil.

A search was conducted to determine what current or proposed standards are available. The search incorporated the Computer-Aided Environmental Legislative Data System (CELDS) of the Environmental Technical Information System (ETIS) at the U.S. Army Construction Engineering Research Laboratory (CERL), Champaign, Illinois. This data base contains current Federal and state environmental legislation. Review of all information available revealed no related standards specifically for soil contamination.

Telephone interviews were initiated with six state environmental agencies: California, Minnesota, Nevada, New Jersey, Pennsylvania, and Wisconsin. These states were identified from a search of hazardous waste regulations conducted for a previous Task Order (contract DAAKI1-82-C-0017, Task Order 3). The purpose of the interviews was to obtain information on proposed standards or criteria and receive insignt on how individual states deal with soil contamination. Table 1 provides a summary of the interviews.

Minnesota standards and California proposed standards are presented in Table 2. These standards are not soil specific. Under these state regulations, soils with concentrations above specified limits are considered contaminated.

Relevant Federal standards, other than the RCRA regulations, are for PCB contamination. The Toxic Substances Control Act has set a PCB overall limit value of 50 ppm.



TABLE 1. SUMMARY OF STATE REGULATIONS RELATIVE TO SOIL CONTAMINATION

State	Criteria/regulations
California	The California Assessment Manual covers soil contamination for the state. A proposed addendum to these hazardous waste regulations is solid waste standards for hazardous waste identification. These standards will be relevant to soils.
Minnesota	The Pollution Control Agency hazardous waste rules apply to soil. Included in these rules are solid waste standards for hazardous waste contamination.
Nevada	Soil contamination is defined as any contaminant present that is not naturally occurring in the soil. RCRA guidelines are followed.
New Jersey	New Jersey is in the process of developing soil contamination standards. It is expected that these standards will be proposed in the fall of 1984.
Pennsylvania	Soil contamination is governed by the solid waste and hazardous waste regulations for the state. Soil criteria are defined from evaluation of specific sites.
Wisconsin	Soil contamination criteria are based on specific evaluation of each individual site.

	Calif		Minnesota		
	Threshold limit concentrationa Wet-weight mg/kg		Hazardous waste		
			ConcentrationD Dry weight		
Contaginant			mg/kg	mg/L	
Concastiant	- 3 ,				
Inorganic compounds	Total	<u>Soluble</u> C	Total	<u>Soluble</u> d	
Antimony	500	100	500	5.0	
Arsenic	500	S			
Asbestos	10,000 10,000	100			
Barium Beryllium	75	7.5	20		
Cadmium	100	ı	500	1.0	
Hexavalent chromium	500	5	1,000	5.0	
Chromium and/or trivalent chromium	2,500	25	1,000	5.0	
Cobalt	8,000 250	80 2.5			
Copper	18,000	180			
Fluoride salts Lead	1,000	5	600	3.0	
Mercury	20	0.2		0.2	
Molybdenum	3,500	350	10.000		
Nickel	2,000	20 1.0	10,000		
Selenium	100 500	5			
Silver Thallium	700	7.0			
Vanadium	2,400	24			
Zinc	2,500	25			
Organic compounds					
2-Acetylaminofluorene (2-AAF)			1,000	0.3	
Aldrin	1.4	0.14	100	0.3	
4-Aminodiphenyl (4-ADP) Benzene			100		
Benzidine			100		
Carbon tetrachloride			100		
Chlordane	2.5		100	0.1	
Chloroform (PCMP)			100		
Bis-(Chloromethyl) ether (BCME) Chloromethylmethyl ether (CMME)			100		
DDT, DDE, DDD	1.0	0.1		0.01	
3,3-Dichlorobenzidine (DCB)			1,000		
2,4-Dichlorophenoxyacetic acid	100	10			
Dieldrin	8.0	0.8	1,000		
4-Dimethylaminoazobenzene (DAB) Dioxin (TCDD)	0.0	,			
Endrin	0.2			0.02	
Ethyleneimine (EI)			1,000		
Heptachlor	4.7	7 0.47 2.1		0.01	
Kepone	4.0				
Lindane Methoxychlor	100	10		0.3	
4,4-Methylene-bis-2 chloroaniline (MOCA)			100		
Mirex	21	21	1 000	0.01	
a-Naphthylamine (1-NA)			1,000 100		
b-Naphthylamine (2-NA) Pentachlorophenol	17	1.7			
Polychlorinated biphenyls (PCB)	12	1.2	500	0.01	
B-Propiolactone (BPL)			1,000		
Toxaphene	2 040	0.5 240		0.05	
Trichloroethylene 2,4,5-Trichlorophenoxyacetic acid	2,040 10	1.0			
Vinyl chloride (VCM)			100		
Explosives-related compounds					
Aniline	***				
N,N-Dimethylaniline					
1,3-Dinitrobenzene					
Dinitrotoluenes Diphenylamine					
4-Nitrobiphenyl (4-NBP)			100		
Nitrocellulose			1 000		
n-Nitrosodimethlamine (DMN)			1,000		
Tetryl					

Threshold limit concentration (total and soluble) - Draft California Administrative Code, Social Security, Division 4, Environmental Health, Chapter 30. Minimum standards for Management of Hazardous and Extremely Hazardous Waste. Criteria for Identification of Hazardous and Extremely Hazardous Wastes, R-45-78, 13 October 1982.

blazardous waste limit concentration (total and soluble) - Minnesota Code of Agency Rules, Hazardous Waste Rules, Section 6MCAR/4.9002- Classification, Evaluation and Certification of Waste, 1982.

CSoluble threshold limit concentrations are based on extract from the waste extraction test procedure outlined in the proposed criteria for the California Assessment Manual. The total soluble fraction of each pertinent component shall be calculated and reported as a concentration in the waste as the total soluble concentration in milligrams per kilogram, where total soluble concentration equals 40 times the concentration of the component, in milligrams per liter, in the combined extractant filtrate.

dSoluble hazardous waste concentrations are based on an extract from the EP Toxicity Method of Test Methods for Evaluating Solid Waste, 40 CFR Part 261.



Currently, regulatory agencies base soil contamination on hazardous waste criteria. Soil is considered contaminated if it contains concentrations of hazardous wastes above the governing hazardous waste criteria.

Since reliable criteria specific to contaminated soil were not available at the time of this study, it was agreed that technology assessment for soil decontamination would be better accomplished by evaluating individual technologies for their inherent performance.



3. TECHNOLOGY IDENTIFICATION AND CHARACTERIZATION

3.1 Selection of technologies. The result of the information search was a list of technologies that can be used for the removal of selected contaminants from soils. The technologies ranged from current state-of-the-art, practiced technologies through alternative technologies (technologies developed for other purposes that may be applicable to the removal of contaminants from soil), to developmental technologies. The list included both generic processes and actual marketed removal technologies. (Some marketed processes may be proprietary.) The identified technologies have conceptual applications for removing heavy metals, explosives, or solvents from soils (these technologies may have the design capabilities for removing a combination of these contaminants).

The technologies fell into four broad categories: thermal, chemical, biological, and physical processes. Tables 3 through 6 list the technologies identified, their current development status, and their anticipated ability to remove metals, solvents, and explosives from contaminated soils. Subsections 3.2 through 3.5 present process descriptions along with corresponding process applicability information.

Technologies were also defined by their current status. A technology was considered state-of-the-art if it had been utilized to remove the identified contaminants from soils either in the laboratory or in field applications. An alternate technology was one that had been utilized to remove an identified contaminant in a nonsoil medium. A developmental technology was one that had not been successfully utilized in a field application to remove an identified contaminant, but was being studied as a possible removal technology.

Several technologies were designated for either on-site or in-situ application. On-site applications were those in which the machinery for decontamination could be located on or close to the contaminated site, but some amount of excavation of the contaminated soils would be required prior to treatment. In-situ applications were those which required no removal or excavation of contaminated soils.



TABLE 3. THERMAL PROCESSES

Technology	Current status	Heavy metals removal	Explosives removal	Solvent removal
Vertical well chemical reactor	AL		х	Х
Multiple hearth incinerator	AL		X	X
Rotary kiln incinerator	SA		X	х
Molten salt incinerator	DV		X	x
Fluidized bed incinerator	AL		X	X
Wet air oxidation	AL		X	x
In-situ vitrification	DV	. X	X	x
Plasma arc torch	AL	X	X	X
Microwave plasma detoxification	DV	X	X	X
Burning/torching	SA		. X	· x
Low temperature thermal decomposition	DV		X	Х
In-situ hot air/steam stripping	DV		X	Х
In-situ microwave heating	DV		Х	х
Laser-initiated thermal decomposition	DV		Х	х
Supercritical water oxidation	DV	X	х	x
High temperature fluid wall reactor	DV	X	х	x

DV = Developmental technology.
AL = Alternate technology.
SA = State-of-the-art technology.



TABLE 4. CHEMICAL PROCESSES

Technology	Current status	Heavy metals removal	Explosives removal	Solvent removal
Sulfur-based reduction	AL	Х	X	
Reduction with sodium borohydride	AL	x	x	
On-site solvent extraction	AL	x	X	x
Solvent extraction - Acurex process	AL			X -
In-situ solvent extraction	DV	x	X	x
Decontamination of soils using the Franklin solvent	DV			X
Free radical oxidation	· AL		. X	X
Free radical oxidation - Enercol oxidation process	DV		X	X
Fenton's reagent	AL		X	X
Base-initiated decomposition	AL	•	X	X
Carbon adsorption	AL		X	X
Ion exchange	AL	x		
Surfactant complexing	AL	x	X	X
Complexing with dithiocarbamate	AL	X		
Philadelphia Quartz (PQ) complexing agent	AL	X		
Complexing with cellulose xanthate	AL	x		

DV = Developmental technology.
AL = Alternate technology.
SA = State-of-the-art technology.



TABLE 5. BIOLOGICAL PROCESSES

Technology	Current status	Heavy metals removal	Explosives removal	Solvent removal
Microbial bioaccumulation of metals	DV	X		
Immobilized cells	AL			X
Vermicomposting	AL		X	X
Composting	AL		X	x
Aerobic biodegradation	SA		X	X
Activated sludgeRotating biological contactorBiopond			ė	
Fluidized bed biological	AL		X	X
Landfarming	AL		X	X
Anaerobic biodegradation	AL		X	X
Anaerobic/aerobic cycling	AL		X	X
Adapted microbial cultures	DV		X	X
Vegetative uptake	DV	X		
Bioreclamation of soils (GDS system)	SA			X

DV = Developmental technology.
AL = Alternate technology.
SA = State-of-the-art technology.



TABLE 6. PHYSICAL PROCESSES

Technology	Current status	Heavy metals removal	Explosives removal	Solvent removal
Secure landfill	SA	X		X
Slurry wall	SA			x
Grouting	SA			x
Geological isolation	DV	x	X	X
Stabilization (chemical admixing)	SA	X		
Microencapsulation	SA	X		
Macroencapsulation	SA	X		
High gradient magnetic separation	AL	X		
Washout	AL		Х	

DV = Developmental technology.
AL = Alternate technology.
SA = State-of-the-art technology.



3.2 Thermal processes.

3.2.1 Vertical well chemical reactor.

3.2.1.1 Description. The vertical well chemical reactor (VWCR) is designed to oxidize sludges and wastewaters having a sufficient organic content. It operates under the same principles as the wet air oxidation unit, except the VWCR is placed in the ground, as illustrated on Figures 2 and 3. Contaminated sludge or wastewater flows down the center tube (downcomer), with effluents leaving the system via the upcomer. Tube diameter and length are calculated so that the necessary reaction time and pressure for the oxidation process can be attained. Air pressurized to 500 psig should be provided to overcome existing static pressure. The air assists the fluid flow through the reactor and provides oxygen for combustion.

The reactor tubes are jacketed to provide heat transfer liquids to heat or cool the VWCR to maintain a proper temperature profile. (Upflowing oxidized waste is gradually cooled as it transfers heat to the downflowing fresh waste.) The VWCR system can be placed in a conventionally-cased oil or gas well. Insulation to minimize heat losses from the VWCR to the surrounding soil should be provided to ensure optimum reaction conditions. The system oxidizes organic wastes into carbon dioxide and water. Some low molecular weight organic matter, such as organic acids, aldehydes, and acetates, will be observed in the effluent.

3.2.1.2 Applicability.

- (a) A VWCR has been constructed in Longmont, Colorado and is currently in operation for oxidizing biological sludge.
- (b) The direct applicability of the system to soils is questionable. Soils in solution could create operational problems due to their inorganic content. This process can treat wastes with a higher solids content than would be treatable by the wet air oxidation process.
- (c) Optimal operation of the system occurs with wastes having a high organic content so that a thermally self-sustaining reaction can be maintained. A contaminant content of 5,000-15,000 ppm chemical oxygen demand (COD) is recommended.
- (d) The interacting effects of metal solubility, adsorption, and desorption have not allowed a definitive conclusion of the fate of metals.

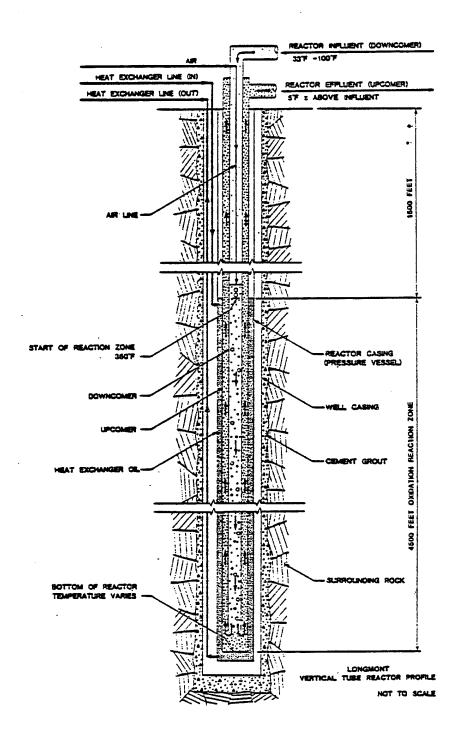


Figure 2. Typical vertical well chemical reactor profile.

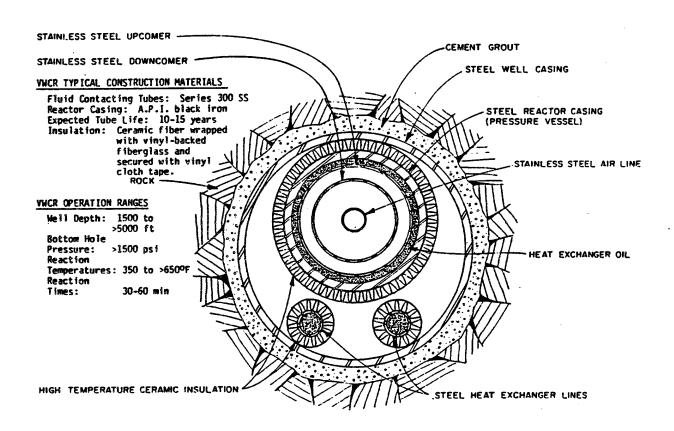


Figure 3. Typical vertical well chemical reactor cross section.



3.2.1.3 Comments.

(a) The effluent may contain low molecular weight organic matter (aldehydes and acids).

(b) The effluent may contain hazardous by-products of explosive oxidation and thermal degradation, such as 1,3,5-TNB or 2,4-DNT.

(c) Corrosion and scale formation in the reactor and heat exchanger tubes are inherent problems of this process. Suspended solids will contribute to erosion of the equipment.

(d) Soil backfill will be necessary to restore the contaminated site.

3.2.1.4 References.

(a) Conway et al., 1980.

(b) EPA Municipal Environmental Research Laboratory, 1982.

(c) Patent No. 4,376,598 held by the Department of Energy.



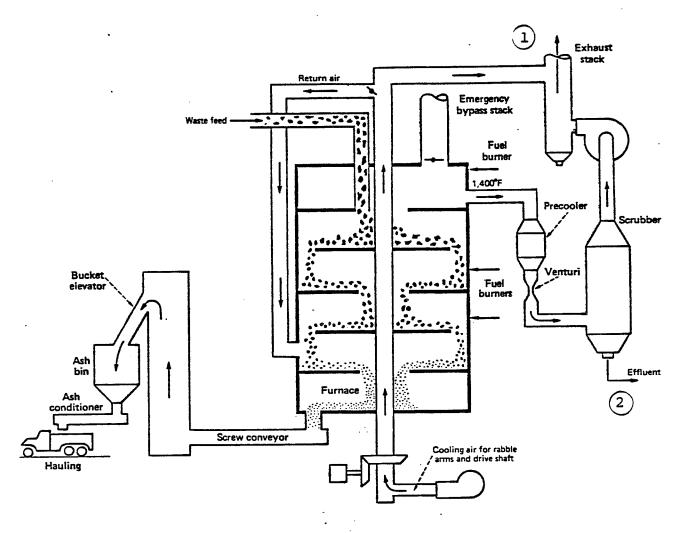
3.2.2 Mutiple hearth incinerator.

3.2.2.1 Description. The multiple hearth incinerator (Figure 4) is designed for the disposal of organic wastes with low heating values via thermal destruction. The multiple hearth incinerator is a cylindrical steel shell lined with refractory material. This chamber is divided into smaller zones, or hearths, which are created by self-supporting refractor arches. The organics-contaminated waste stream is fed via gravity through a feed port at the top of the incinerator. Rabble arms and teeth, attached to a vertically-positioned central shaft, rotate to spiral the waste stream across the hearths and through the furnace. The contaminant drops from hearth-to-hearth through passages alternately located either along the periphery of the hearth or adjacent to the central shaft.

Waste retention time is controlled by the design of the rabble tooth pattern and the speed of the central shaft. Retention times are usually between 15 and 90 minutes with temperatures of 1,400 to 1,800°F. Exhaust gases from the unit may be passed through a waste heat recovery unit, and then to a venturi-type scrubber and a cyclone separator to remove the fine particulates. An afterburner may be necessary to destroy any organics that were vaporized but not destroyed in the incinerator. Inorganics and any partially combusted organic material are collected at the bottom of the hearth and are transported to the disposal area.

3.2.2.2 Applicability.

- (a) This technology has been commercialized for solids incineration.
- (b) The system can successfully incinerate granular, homogeneous soil feed, although there is no reported experience in processing explosives-contaminated soil.
- (c) The system is likely to be energy intensive.
- (d) The system has been installed to incinerate waste biological sludge and chemical manufacturing residues at a large petrochemical plant in the South.
- (e) The system is not suitable for mobile applications.
- (f) The system can operate with media consisting of organics and inorganics. Inorganics leave the system as ash.



Source: Hitchcock, 1979

Figure 4. Typical multiple hearth incinerator system (without afterburner).



3.2.2.3 Comments.

- (a) Ash from this process may contain hazardous by-products if used for explosives-contaminated soil (2,4-DNT or 1-3,5-TNB).
- (b) Effluent gas may contain NOx.
- (c) Liquid effluent from a Venturi scrubber may contain low weight organics (aldehydes and organic acids).
- (d) Soil backfill will be necessary at contaminated sites.
- (e) The system can be operated under oxygen-starved (pyrolytic) conditions. Pyrolysis would be employed when the waste material has a high calorific content (containing a gross Btu to moisture ratio greater than 3,500 Btu per pound of water (Hitchcock, 1979)).

3. 2. 2. 4 References.

- (a) Beauclet et al., 1983.
- (b) Coia et al., 1983.
- (c) Malarkey et al., 1979.
- (d) Hitchcock, 1979.



3.2.3 Incineration with a rotary kiln.

3.2.3.1 Description. Rotary kiln incinerators are versatile units that have sufficient design flexibility to ensure thermal destruction of organic contaminants. The organics-contaminated waste stream is fed into a rotary kiln, which is a cylindrical horizontal shell mounted at a slight downward incline (Figure 5). A typical rotary kiln is designed with a length 2 to 10 times the diameter, and a rotational speed of 1 to 5 rpm. Operating temperatures are between 1,500 to 3,000°F. Design parameters are dependent on the contaminant and the nature of the waste stream.

Excess air is used to ensure complete combustion. Ash and nonoxidized materials are collected and are either returned to the original site or are removed for disposal. Most kiln systems are designed with an afterburner to permit complete destruction of all contaminants (materials that were volatilized but not combusted in the kiln). Effluent gas is cooled, passed through a scrubber to remove particulates, and then released to the atmosphere.

3.2.3.2 Applicability.

(a) The kiln system is available commercially.

(b) USATHAMA will conduct test burns with a rotary kiln (September 1983) using explosives—contaminated lagoon sediment from two Army installations. The process will be demonstrated at operating conditions of 800°F to 2,200°F and 0.2 rpm.

(c) A modular rotary kiln system has been developed by EPA

research, Edison, New Jersey (Figure 6).

(d) This system is applicable for the treatment and destruction of most organics. Most inorganics are not affected by this process and will leave the system as ash, or in the exhaust system.

3. 2. 3. 3 Comments.

(a) Eftluent gas should contain no hazardous by-products, assuming an afterburner is used.

(b) Effluent ash may contain hazardous components such as heavy metals and thermal degradation by-products of explosive compounds.

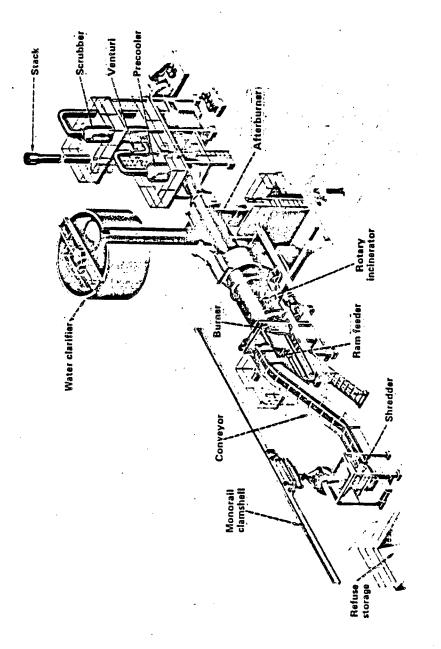


Figure 5. Typical rotary kiln incinerator system.

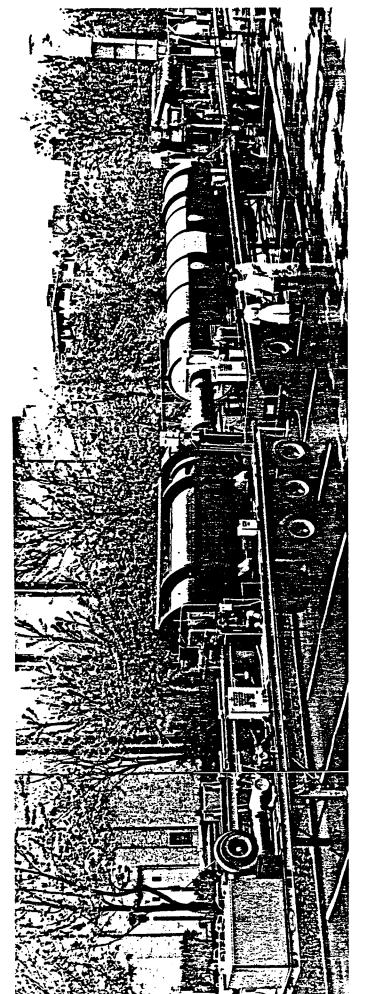


Figure 6. Mobile rotary kiln incinerator.

23



3. 2. 3. 4 References.

- Weston, Roy F., Inc., Test, 1983. "Test Plan for an Incinerator (a)
- Pavoni et al., 1975. (b)
- Wentsel et al., 1981. Hitchcock, 1979. (C)
- (d)
- Ryser, 1983. (e)
- Personal communication with Rich Traver, EPA, Edison, (f) New Jersey, 1 July 1983.



3. 2. 4 Molten salt incinerator.

3.2.4.1 Description. Incineration is a thermal degradation process in which organic contaminants are decomposed via high temperature oxidation to a less bulky, nonhazardous residue. In the molten salt process, shown on Figures 7 and 8, a medium containing approximately 90 percent sodium carbonate and 10 percent sodium sulfate is utilized to provide operating temperatures between 1,500 and 1,800°F. Substitution of other salts, such as K2CO3, can lower the operating temperature. The use of eutectic mixtures (e.g., NaOH-KOH, Li2CO3) can provide the additional benefit of entrapping potentially toxic or objectionable off-gas constituents (e.g., heavy metals such as mercury, lead, cadmium, arsenic, and selenium).

The molten salt incinerator is operated at a lower temperature than the other types of incinerators. This minimizes the nitrous oxides that are formed at high temperatures. Organics burn completely, producing steam and carbon dioxide. Inorganic impurities, such as chlorine, will react with the salt; the resulting nontoxic ash must be disposed of.

The spent salts can often be regenerated for reuse in the process. Depending on the organic content of the waste, supplemental fuel (oil, gas, coal) may be required to carry out the process.

3.2.4.2 Applicability.

- (a) Molten salt incineration was originally devised to destroy DDT and mustard gas, but recent EPA studies have confirmed its suitability for toxic solvents and acids. Current interest centers around the capability of the treatment for PCB destruction.
- (b) The process is suitable for the treatment of organic residues that can be fed directly into the incinerator either as free-flowing powder or shredded materials.
- (c) Liquids and slurries are usually sprayed into the incinerator with combustion air.
- (d) This process is suitable for on-site treatment of contaminated soils, extracts, and slurries.
- (e) A commercial incinerator marketed by Rockwell International can treat 1 ton of waste per hour. Transportable models destroy 10 to 250 pounds of waste per hour.



3.2.4.3 Comments.

The waste volume is reduced to less than 1 percent of its original volume for wastes high in organic content.

3. 2. 4. 4 References.

- (a) Piasecki, 1983.
- Malarkey, 1979. Hitchcock, 1979. (b)
- (c)
- Kiang and Metry, 1982. (d)

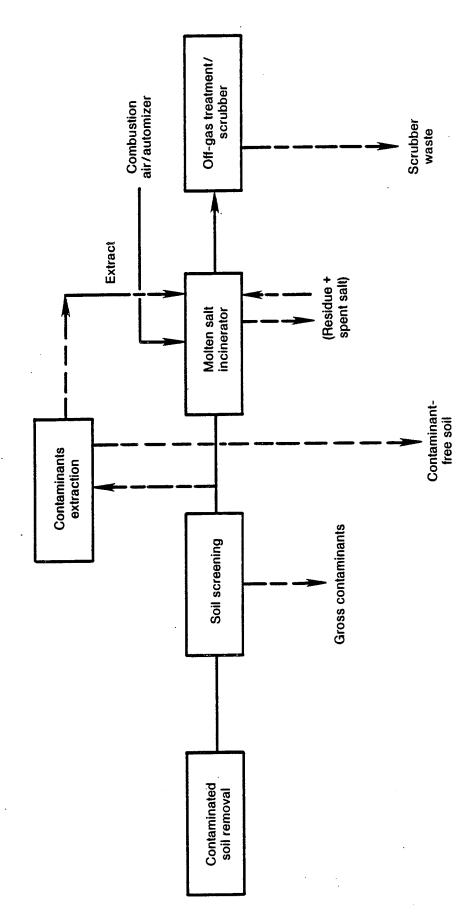
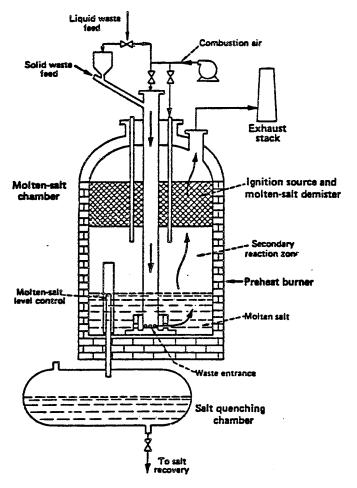


Figure 7. Process flow diagram - molten salt incinerator.



Source: Kiang and Metry, 1982

Figure 8. Schematic diagram - molten salt incinerator.



3.2.5 Fluidized bed incinerator.

3.2.5.1 Description. The fluidized bed incinerator system will chemically oxidize organics via thermal degradation. This incinerator, shown on Figure 9, consists of a vertical refractory-lined vessel containing a bed of inert granular material. Combustion air is introduced at the bottom of the vessel and rises through the bed. The upward flow of air results in turbulent mixing and causes fluidization of the bed. Waste material is fed into the bed and combustion occurs. Inorganic materials that may remain after incineration can become the bed for future waste feeds.

The vigorous mixing provided by the air promotes combustion of the waste material. Auxiliary fuel is usually provided to maintain a temperature high enough to ensure destruction. Fluidized beds usually consist of sand or aluminum oxide. The feed may be aqueous, slurry, or solid phase. The incinerator may operate at temperatures approaching 2,200°F.

3.2.5.2 Applicability.

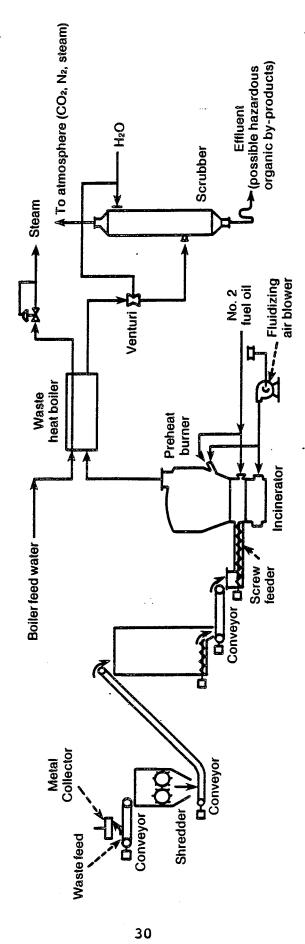
- (a) The system is available commercially.
- (b) The system has been successful in destroying organics in the liquid/solid phase.
- (c) A 10-percent TNT slurry was successfully destroyed using this system (Tatyrek, 1976).
- (d) There is no reported experience for decontamination of soils in a fluidized bed incinerator.
- (e) Mobile (trailer-mounted) or transportable units are not currently available.
- (f) Most inorganic contaminants are not affected by the process.
- (g) An afterburner may be necessary to ensure the destruction of volatilized organic contaminants.

3.2.5.3 Comments.

- (a) Aqueous effluent may contain hazardous by-products although this is not indicated in published literature.
- (b) Gaseous effluents should be treated to reduce particulate and vapor emissions to the atmosphere.

3.2.5.4 References.

- (a) Hitchcock, 1979.
- (b) Tatyek, 1976.
 - (c) Shapira et al., 1977.



Typical fluidized bed incinerator system. Figure 9.

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Source: Hitchcock, 1979



3.2.6 Wet air oxidation (WAO).

3.2.6.1 Description. Wet air oxidation is an aqueous phase oxidation of low concentrations of dissolved or suspended organic substances at elevated temperatures and pressures. Water, which usually makes up the bulk of the aqueous phase, serves to modify the oxidation so that it proceeds at temperatures of 175 to 325°C. Water also controls the oxidation rate by removing excess heat by evaporation, and provides an excellent heat transfer medium. This enables the wet oxidation process to be thermally self-sustaining, even with the relatively low organic feed concentrations.

Oxygen required for the reaction is obtained using pressurized air. The process pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase (300 to 3,000 psig). Catalysts may be used to enhance the rate of oxidation. The process is suitable for treating wastes containing suspended solids (usually no more than 3 to 5 percent).

The wet air oxidation process is shown on Figure 10. The waste stream is fed via a high pressure pump to a heat exchanger. Here the waste stream is preheated using the hot oxidized reactor effluent and fed into the reactor. (The pump and preheater establish wet air oxidation reaction conditions.) As oxidation progresses up through the reactor, combustion neat is liberated, increasing the temperature of the reaction mixture. The gas and liquid phases are separated after leaving the reactor. The liquid is cooled in the reactor preheater, and can be discharged, treated further, or processed for recovery of by-products.

3.2.6.2 Applicability.

(a) The process is available commercially; pilot-scale equipment is available for testing.

(b) The process is applicable for the treatment of aqueous slurries containing organic contaminants (minimum COD-15,000 ppm for thermally self-sustaining reactions).

(c) The treatment of contaminated soils has not been demonstrated. It is assumed that the soils will be slurried before treatment.

(d) The system can be used in conjunction with other treatment processes to fully decontaminate a waste stream. WAO will not affect inorganics.

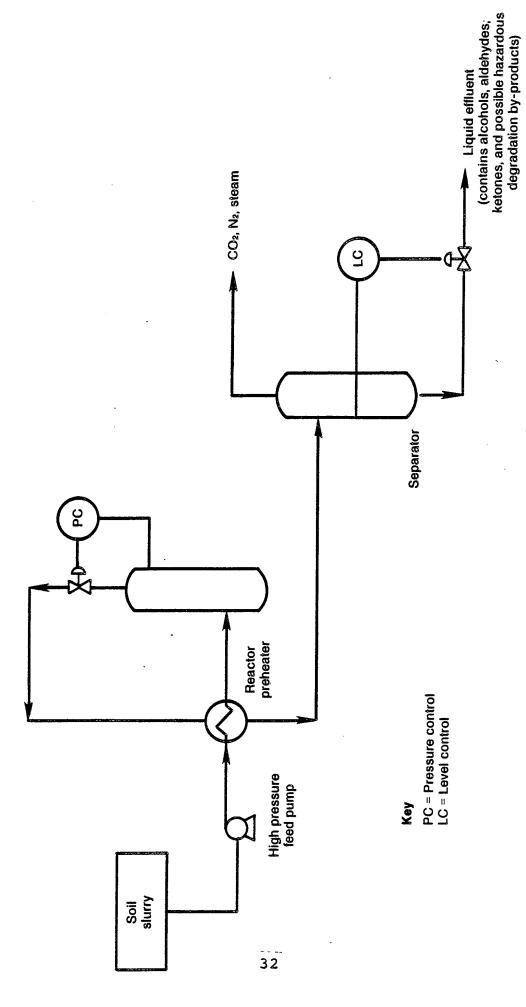


Figure 10. Wet air oxidation - process flow diagram.



(e) Tests with explosives indicate that RDX, HMX, and tetryl degrade into nontoxic substances, but TNT degrades to the toxic 1,3,5-TNB as its end product (Wentsel, 1981).

(f) Nonchlorinated organics have been completely degraded into nontoxic products. Aliphatic hydrocarbons are oxidized into alcohols, aldehydes, and ketones, which

are readily biodegraded.

(g) Zimpro, Inc. has developed a skid-mounted, portable wet air oxidation unit that handles a flow rate of 10 gpm.

3.2.6.3 Comments.

- (a) Oxidized liquid effluent from systems may contain hazardous degradation products, and may require further treatment (e.g., biological treatment to remove any organic degradation products).
- (b) This process should not be energy-intensive, assuming minimum COD feed requirements are maintained. Heat contained in the oxidized product can be harnessed to produce steam and hot water.

3.2.6.4 References.

- (a) Beaudet et al., 1983.
- (b) Paulson, 1977.
- (c) Conway et al., 1980.
- (d) Pavonic et al., 1975.
- (e) Pradt, 1972.
- (f) Wentsel et al., 1981.
- (g) Industrial pollution control systems, Zimpro, 1983.



3.2.7 In-situ vitrification.

3.2.7.1 Description. The in-situ vitrification process involves melting organic and inorganic contaminants and the surrounding soil and rock in place to form a durable glass or crystalline product. Vitrification is accomplished by placing 30- to 40-foot long electrodes in the soil around the contaminated site. The position of the electrodes determines the area and volume vitrified. Presently a full-scale unit is proposed that would have four electrodes placed in an 18-foot square, as shown on Figure 11. The system will draw 450 amps at 4,160 volts. The power would be fed for 120 hours to ensure vitrification of the volume between the electrodes. Electric current is passed between the electrodes to produce the 2,500°F temperature necessary to begin melting.

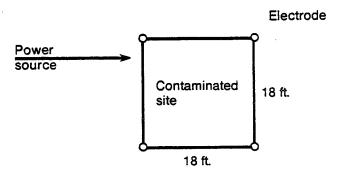
The heat decomposes organic materials and dissolves or encloses inorganic material. As the molten material cools, it forms a glass block. Tests of the process have found no movement of hazardous material into the surrounding soil. Battelle estimates that the process can decontaminate 100 tons of soil per day. If necessary, a dome could be placed over the area being vitrified and any gases generated could be passed through a scrubber to remove volatile hazardous components (unidentified-dependent on soil composition and resultant decontamination by-products) before being vented to the atmosphere.

3.2.7.2 Applicability.

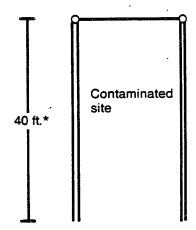
- (a) This technology has been tested on a pilot scale. Batelle appears ready to commercialize the process.
- (b) The technology has the potential to decontaminate all wastes (by immobilization).
- (c) Future land use questions have not been fully answered since the process has not been commercially field tested.

3.2.7.3 Comments.

- (a) Possible hazardous gaseous by-products may be a result of this treatment process.
- (b) Cost information: \$90 to \$130/cubic yard (Battelle estimate).



Typical vitrification cross section.



*Length of electrode.

Typical vitrification profile.

Figure 11. Proposed full-size vitrification unit.



3.2.7.4 References.

- Chemical Engineering, 25 July 1983. (a)
- (b)
- Patent No. 4,376,598 held by the Department of Energy. Personal communication with Jim Beult, Battelle NW La-(C) boratories, 19 September 1983.
- Ona et al., 1982. (d)



3.2.8 Plasma torch.

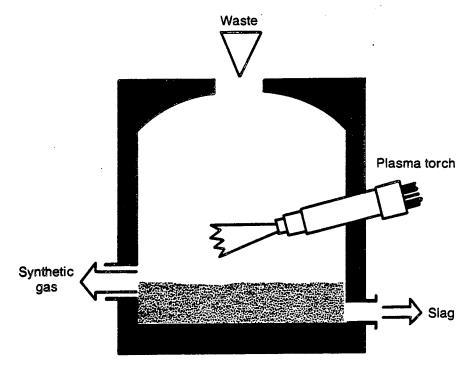
3.2.8.1 Description. The plasma torch can detoxify both organic and inorganic wastes in both solid and liquid states. This device utilizes an electrical discharge to change minute quantities of almost any gas into an extremely hot sustainable flame (reported to be $100,000^{\circ}F$).

The gas, which can be an oxidizing, reducing, or inert substance, is introduced into the plasma arc reactor (Figure 12) to create a swirling motion that keeps the plasma flame in the center of the torch away from metal parts. An electrical discharge is established (plasma arc flame) and maintained between the electrode inside the torch and any internal electrical conductor. The electrical energy of the flame is converted to the heat energy of the plasma.

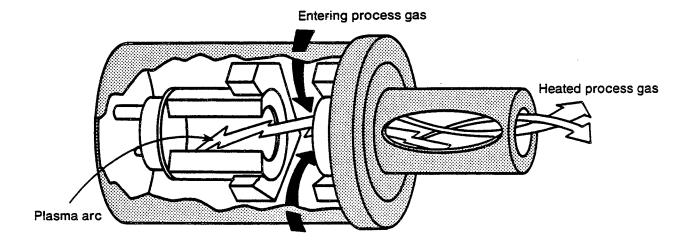
The waste stream is fed into the reactive zone of the plasma torch. At this point high energy electrons bombard the waste material, breaking molecular bonds and rearranging the substances to basic elements (typically carbon, hydrogen, oxygen, and chlorine). Potentially hazardous gases must be fed to a scrubber where they may be neutralized. Metals can be recovered in their pure form (this has been demonstrated in pilot work by SKF Steel Engineering Co. in Sweden) if they exist in the incoming waste stream. The remaining inorganics leave the system as a slag. Energy can be recovered from the gaseous by-products that are produced.

3.2.8.2 Applicability.

- (a) The technology has been demonstrated on a commercial scale for metals recovery from used ores.
- (b) Plasma arcs were developed by the National Aeronautics and Space Administration (NASA) to test materials at the temperatures encountered during reentry into the atmosphere.
- (c) A portable plasma arc generator has been developed by Tom Barton, a Canadian engineer with no apparent corporate connections.
- (d) The system has been tested with solids.
- (e) A plasma torch has not been tested with explosives.
- (f) The system has successfully treated liquids contaminated with 65 percent PCB's (Bartow, 1980).
- (g) SKF Steel Engineering Co. in Sweden has developed a plasma torch unit that is used to recover zinc, lead, and iron from steel-making dust (Figure 13).
- (h) USATHAMA is researching the plasma torch as a technique for destroying obsolete nerve agents.



Source: Kiang, 1982



Source: Chemical Engineering, 5 September 1983

Figure 12. Plasma arc reactor schematic.

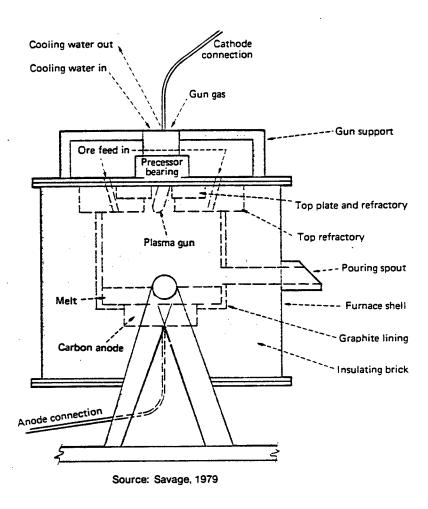


Figure 13. Cross section of a plasma arc furnace.



- (i) Westinghouse Electric Corporation has just opened a new facility at its Waltz Mill site in Madison, Pennsylvania to develop the plasma torch for industrial applications.
- 3.2.8.3 Comments.
- (a) Product gas may contain organics that have not fully decomposed.
- (b) Slag may contain hazardous inorganic compounds that will require disposal at a secure landfill.
- 3.2.8.4 References.
- (a) Piasecki, 1983.
- (b) Chemical Engineering, 5 September 1983.
- (c) Krishnan, 1983.
- (d) Savage, 1979.
- (e) Bartow, 1980.



- 3.2.9 Microwave plasma detoxification.
- 3.2.9.1 Description. Microwave plasma is an ionized gas (may be inert or other) produced via microwave-induced electron reactions with neutral gas molecules. In a gas under reduced pressure (100 to 200 torr), a few low energy electrons are accelerated by the microwave electromagnetic field causing collisions with other gas molecules and generating additional charged ions. The continuation of this process forms a plasma.

By operating under these conditions it is possible to maintain the free electrons at high temperatures without heating the bulk gas. The system's mechanism is principally electronic, rather than thermal, so low equipment temperatures can be maintained, thus reducing the cost of the materials of construction. In addition, the systems are leak-tight due to the vacuum requirements, resulting in a high level of safety in operation.

The system may produce hazardous by-products (this depends on the gas used as a plasma generator).

- 3.2.9.2 Applicability.
- (a) The system has been tested for decomposition of toxic gases used by the U.S. Army in a laboratory-scale operation.
- (b) Equipment has been developed with a waste stream feed capacity of 30 pounds/hour.
- (c) This system has been shown to be highly effective for the detoxification/destruction of hazardous organic wastes, including PCB's, methyl bromide, and polyaromatic dye mixtures.
- (d) No experience with soils has been reported.
- 3.2.9.3 Comments.
- (a) Toxic materials may result from contaminant degradation. The actual products depend on the contaminant, as well as the gas used as the plasma. These materials leave the system as both gases and solids.
- (b) Cost information (June 1978): Capital cost: \$100,000 per unit (50 pounds/hour capacity); operating cost for detoxification of phenylmercuric acetate solution: \$380 per ton.
- 3.2.9.4 References.
- (a) Beneche et al., 1983.
- (b) Bailin et al., 1975.
- (c) Bailin et al., 1976.
- (d) Shapira et al., 1977.



- 3.2.10 Burning/torching.
- 3.2.10.1 Description. This process involves incineration of organics-contaminated soil by in-situ ignition. For successful completion of this process the soil must be able to sustain combustion (based on the Btu value of organic contaminants and their volumetric quantity in the soil). This process should completely oxidize organic contaminants to carbon dioxide, water, or nitrous oxides. The process may be aided by applying a flammable liquid to the contaminated soil before torching.

Hazardous by-products are possible. No interference from nonorganic contaminants is expected.

This process may also be implemented on-site by excavating the soil before igniting it. A temporary dome structure may be placed around the contaminated site so that gaseous products may be collected and treated to remove any hazardous low temperature thermal degradation by-products.

- 3.2.10.2 Applicability.
- (a) Metals and other inorganics will remain in the soil as ash.
- (b) It is known that some contaminated soils on Army depots have ignited. The process is limited by the flammability of the contaminated soil and the difficulty of actual system process control.
- (c) The depth of penetration is limited to surface applications.
- (d) The possibility of explosion does exist, especially if explosives are concentrated in pockets.
- 3.2.10.3 Comments.
- (a) Hazardous by-products may result from burning soil.
- 3.2.10.4 References.
- (a) Shapira et al., 1977.



- 3.2.11 Low temperature thermal decomposition.
- 3.2.11.1 Description. Explosive organic contaminants will decompose, without detonation, when subjected to temperatures that are lower than incineration temperatures. The degradation is carried out at 100 to 350°C, and 350 psia, and the products are usually volatile species.

Decomposition data are known, and rate expressions have been derived, showing reaction rate as a function of temperature. The decomposition is exothermic, and may be autocatalyzed by the products. Ultraviolet radiation, methanol and certain waxes were also found to have a catalytic effect.

Possible methods for thermal decomposition include microwave, infrared or convective heating (ovens), hot gases, contact heating (electrical coils), and controlled burning/solvent soak. Treatment may be on-site or in-situ.

3.2.11.2 Applicability.

- (a) Decomposition data for RDX, HMX, TNT, DNT, NC, NG, NQ, and tetryl indicate safe decomposition at lower temperatures. The time frame ranges from 1 second to 1 year, depending on temperature. All data are based on studies with pure, dry explosives; it is unknown if explosives in soils exhibit the same behavior.
- (b) Only TNT had hazardous products, nitroaromatics, but these can be thermally treated for further degradation to nonhazardous end products.
- (c) Thermal degradation of explosives in lagoon sediments is currently being investigated for USATHAMA by ESE.
- (d) Thermal treatment does not affect metals, which will remain in the soil.
- (e) Major end products from the decomposition of explosives include CO, CO₂, NO_X, N₂, H₂O, CH₂O, HNO₃, C₂H₂O, and HCON(OH)Me.

3.2.11.3 Comments.

- (a) The explosives' sensitivity to detonation depends on the concentration. Therefore, pockets of explosives pose a hazard, as does excessive drying of the soil.
- (b) This process is controlled by using moderate heat-up rates and reaction inhibitors (products $\rm H_{2}O$ and $\rm NO_{2}$ are inhibitors).
- (c) This process could possibly be adapted for the treatment of solvents.



- 3.2.11.4 References.
- (a) Beaudet et al., 1983.(b) Benecke et al., 1983.



- 3.2.12 In-situ hot air or steam stripping.
- 3.2.12.1 Description. An air/steam sparger can be buried in an organics-contaminated site, as shown on Figure 14. Hot air/ steam will be delivered to the sparger where it is then transmitted to the soil. The gaseous media will then rise through the soil. Contaminants will be thermally decomposed, or in the case of some explosives, may melt. Volatile organics in the soil will be stripped as a gas to the atmosphere. The system will be operated at specific reaction conditions that ensure decomposition of the contaminants present. Other sources of hot air/steam may be used as a heat source (i.e., burner exhaust).
 - 3.2.12.2 Applicability.

87

- The technology should be effective in removing volatile (a) organics.
- The system has not been tested on contaminated soils. (a)
- Treatment will be ineffective in decontaminating inor-(C) ganic metallic compounds.
- Treatment conditions may cause explosions in contami-(d) nated sites.
- 3.2.12.3 Comments.
- Vapors in steam may be hazardous.
- Steam/hot air treatment may result in the movement of (b) hazardous compounds into the groundwater. Some type technology may be required to of containment prevent contaminant migration.
- 3. 2.12. 4 References.
- Shapira et al., 1977. (a)
- King, 1971. (b)

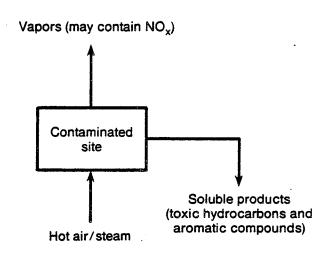


Figure 14. Typical in-situ hot air/steam stripper.



3.2.13 Microwave heating.

3.2.13.1 Description. A beam of microwave energy is directed into the organics-contaminated waste. Microwaves are relatively short electromagnetic waves (wave length between 1 and 100 centimeters) with limited penetrating ability. The microwaves rapidly heat the soil to the temperatures needed for low temperature thermal degradation. This process is shown on Figure 15.

Heat conduction is not an important heat transfer mechanism in microwave heating.

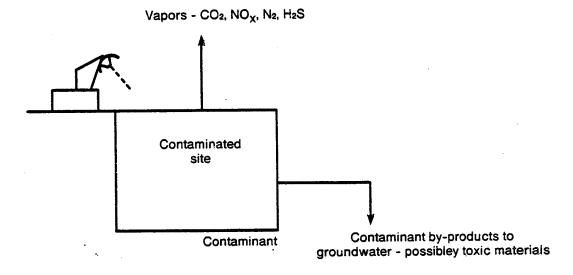
This process can be performed on-site with excavated soils, or may be adaptable to in-situ treatment. Deeper soils, if contaminated, would be treated after the desensitized upper soil layers were removed. The feasibility of in-situ treatment depends on the depth of contamination, reaction by-products, and the microwave penetrating ability in the specific geological formation.

3.2.13.2 Applicability.

- (a) This process has been successfully tested in the laboratory to remove explosives from standard munitions. Tests on contaminated soils have not been reported.
- (b) Equipment is available to perform field tests.
- (c) There is the possibility of an explosion; one such event has been reported.
- (d) Pockets of pure explosives may melt and migrate into the groundwater.
- (e) Most explosives decompose rapidly at their melting points (200 to 280°C). DNT, TNT, and tetryl require higher temperatures, i.e., above 300°C. Decomposition data are available except for TNT and NQ.
- (f) Foreign metal objects (such as nails and screws) will be heated and will decrease the heat-up rate slight-ly. However, inorganic contaminants should not interfere with microwave treatment and will probably be unaffected by the treatment.
- (g) Gaseous decomposition products include NO_X , H_2S , CO, CO_2 , N_2 , HCN, CH_2O , H_2 , and H_2O . The hazardous products would have to be collected for further treatment.



- 3.2.13.3 Comments.
- (a) Certain organics or organic decomposition products may volatilize but not degrade. Vapors may need to be collected for further treatment.
- (b) Microwave radiation energy may possibly be sufficient to desorb compounds from the soil.
- 3. 2.13.4 References.
- (a) Shapira et al., 1977.
- (b) Benecke et al., 1983.



In-situ treatment

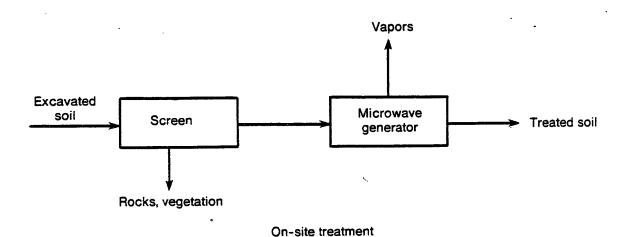


Figure 15. Soil decontamination using microwave heating - process flow diagram.



3.2.14 Laser-initiated thermal decomposition.

3.2.14.1 Description. A CO₂ laser is used to direct an infrared light beam onto a contaminated surface to initiate direct thermal decomposition of surface contaminants. Subsurface contaminants would be thermally decomposed by heat conduction from the irradiated surface. The 1 to 5 kilowatt laser would be centrally located in the area to be decontaminated, and a complex beam guidance system would direct the laser and control its residence time in a specific area. Decontamination time depends on beam diameter, scan rate, and the sophistication of the guidance system. The deeper contaminated soils could be treated after the desensitized soil closer to the surface has been removed.

3.2.14.2 Applicability.

- (a) Theoretically, complete decomposition of all explosives is achievable at elevated temperatures. Except for DNT and TNT, the explosives will rapidly decompose at their melting points (200 to 280°C). DNT and TNT may require heating to higher temperatures (300°C +) to cause rapid decomposition.
- (b) Except for DNT and nitroguanidine (NG), the thermal decomposition of explosives has been fairly well characterized in the scientific literature.
- (c) This system should be successful in removing organics from a contaminated medium.
- (d) Decontamination of soils by laser-initiated thermal decomposition has not been demonstrated.
- (e) The effect of high temperatures on soil structure, composition, and moisture content is unknown.
- (f) Decomposition of explosives by the laser-powered homogeneous pyrolysis technique (LPHP) has been demonstrated.

3.2.14.3 Comments.

- (a) Explosives thermally decompose by ring-splitting or fragmentation to volatile products. Primary products for complete thermal decomposition of explosives include NO, NO2, N2O, N2O, CO2, H2, and H2O. Toxic gaseous products must be scrubbed before release into the atmosphere.
- (b) The primary explosives thermally decompose, forming lead salts (Pb(OH)₂, PbCO₃, etc.).
- (c) The extent of volatile penetration by thermal diffusion is unknown.



- (d) Capital outlay and operating costs per unit volume of soil treated would probably be high.
- 3.2.14.4 References.
- (a) Benecke et al., 1983.



3.2.15 Supercritical water oxidation.

3.2.15.1 Description. The supercritical water oxidation process is capable of oxidizing all organic wastes via thermal destruction using supercritical water (SCW) as the processing media. The contaminated feed waste stream must be either aqueous or slurried to a 5 to 10 percent (by weight) mixture. The solution is pressurized and heated to attain supercritical conditions (500°C and 4,000 psi). This process is shown on Figure 16.

Heating is obtained by mixing the feed with SCW generated in a subsequent step. During a short residence time (less than 2 minutes) in the tube leading to the oxidizer, organics in the feed are converted to combustible gases, low to intermediate molecular weight organic compounds (aldehydes, alcohols), and inorganic salts. Air is pressurized and mixed with the feed. Since the water is supercritical, the oxidant is completely miscible with the solution.

Since the oxidizer operates adiabatically, the heat released by combustion of readily oxidized compounds is sufficient to raise the fluid phase to a temperature at which all organics are oxidized rapidly. The effluent from the oxidizer is fed to a salt separator where the inorganics originally present in the feed are removed as a solid slurry (at 500°C the solubility of inorganics in SCW is extremely low). A portion of the superheated SCW is recycled to an eductor upstream of the oxidizer heat inlet. Off-gas product can be used for power generation.

3.2.15.2 Applicability.

- (a) This system has been tested in a laboratory-scale operation.
- (b) The system is said to be applicable to solids and sludges; however, no tests have been reported with contaminated soil.
- (c) The system can treat organic and inorganic wastes; inorganic salts and heavy metals do not interfere with the process.
- (d) Chlorinated aromatics, benzene, and 2,4-DNT in solution have been successfully oxidized with this system (Modar, Inc., 1982).

3.2.15.3 Comments.

(a) Inorganics entering this system will exit in solid form, most likely as salts, and must be separated and disposed of.

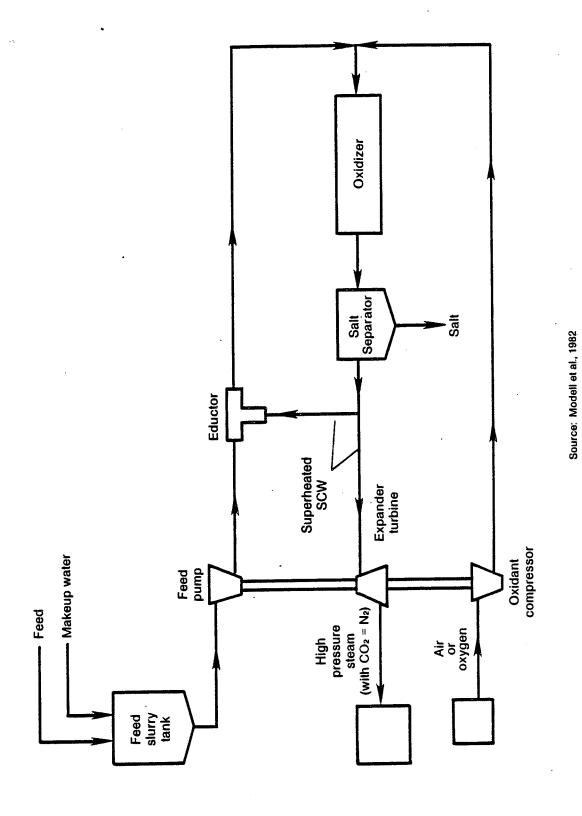


Figure 16. Supercritical water oxidation - process flow diagram.



3.2.15.4 References.

- (a)
- Beaudet et al., 1983. Modell et al., 1982. Josephson et al., 1982. (a) (c)



3.2.16 High-temperature fluid wall (HTFW).

3.2.16.1 Description. The high temperature fluid wall reactor, shown on Figures 17 and 18, is being developed by J. M. Huber, Inc. to detoxify solid wastes via thermal destruction. Contaminated waste material is gravity fed into a porous tube that uses electrical heating elements to radiate thermal energy. Inert gas, usually N2, is forced through the tube creating a fluid wall so that there is essentially no physical contact between the tube and the feed material. This reduces operational problems and ensures longer equipment life. The reactor operates in a nitrogen atmosphere at 4,000 to 5,000°F at low pressures. Waste material is brought to this temperature in a fraction of a second, and the chemicals are broken down into their atomic constituents. The treated soil becomes a nonhazardous, sand-like material.

3.2.16.2 Applicability.

- (a) The system is available in pilot scale for testing various soils.
- (b) This system will decontaminate both organics via degradation and inorganics via vitrification.
- (c) The system has been tested with PCB-contaminated soil for EPA certification (August 1983). Receipt of EPA certification is expected in the fourth quarter of 1983.
- (d) A 50,000 ton/year capacity reactor is currently being designed for commercial application. The system is expected to be modular, not trailer mountable.

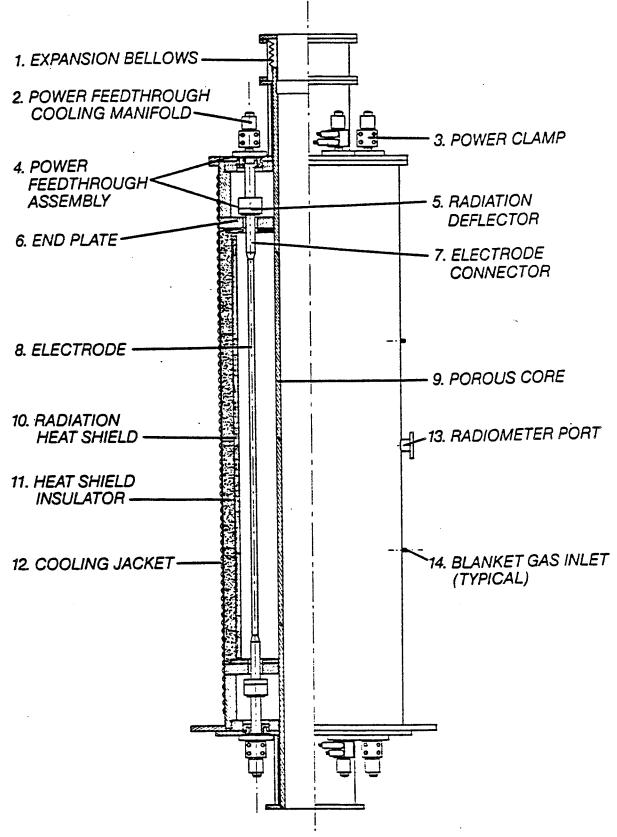
3.2.16.3 Comments.

- (a) Any waste material from this process is likely to be nonhazardous due to the high reaction temperatures that minimize side reactions (U.S. Office of Technology Assessment).
- (b) Gaseous products may need treatment to reduce particulate and vapor emissions.
- (c) The system is likely to produce low to medium Btu synthetic gas when handling organic contaminants, thus reducing energy costs.
- (d) The treated effluent from the system may be returned to the original contaminated site.
- (e) Cost estimate by Huber: \$300 to \$1,500/ton (August 1983).
- (f) Process is patented by Huber.



3.2.16.4 References.

- (a) Personal communication with Oscar T. Scott, IV, J. M. Huber, Inc., 1983.
- (b) Huber Technology Fluid Wall (HTFW) Reactor, J. M. Huber, Inc.



Source: Huber Technology Fluid Wall (HTFW) Reactor, 1983

Figure 17. Profile of a high-temperature fluid wall reactor.

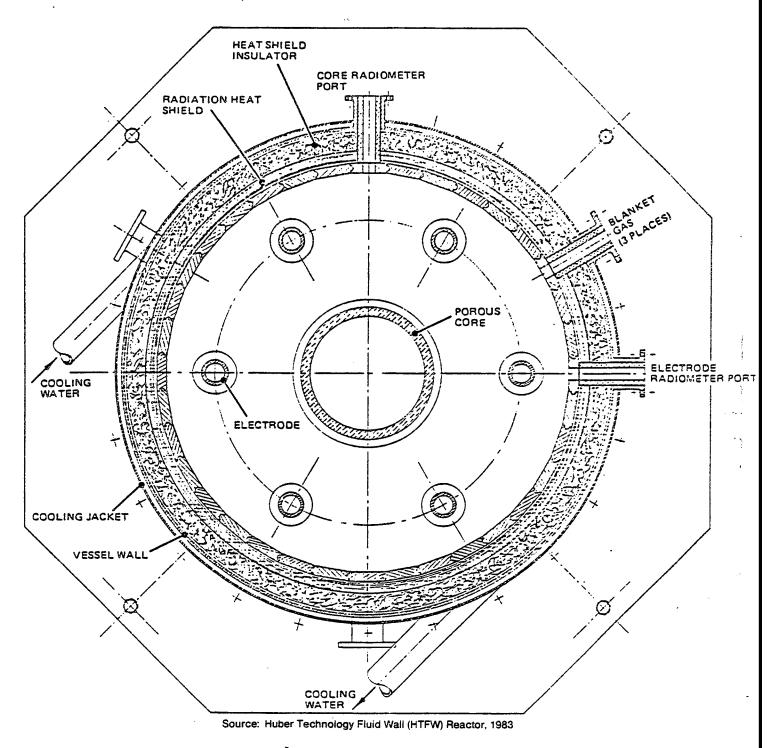


Figure 18. Cross section of a high-temperature fluid wall reactor.



3.3 Chemical processes.

- 3.3.1 Sulfur-based reduction (sulfide precipitation).
- 3.3.1.1 Description. Sulfide-based reducing agents (sodium sulfide, sodium bisulfide) can be used to reduce the nitro groups (R-NO₂) of explosives to amino groups (R-NH₂), as shown on Figure 19(a). The amino groups are nonexplosive but are not always nontoxic. Aromatic amines result from TNT sulfurbased reduction. Sulfur reduction is also an effective process for the treatment of industrial wastes containing toxic heavy metal compounds. In this process the high reactivity of sulfides with metal ions and the very low solubilities of metallic sulfides over a broad pH range result in a high degree of metals removal.

The system can be developed for in-situ or on-site applications. By performing sulfide precipitation in-situ, mobile metals are precipitated as highly immobile sulfides. Explosives are reduced to water-soluble organics or aromatic amines.

On-site sulfide treatment (Figure 19(b)) would require excavation of the contaminated site and repeated washes with sulfide solutions along with water washes. This would elute the amino and amine groups since both are very soluble in water. The metal sulfides formed in the process remain fixed in the soil. The onsite reactions can be controlled more effectively because better contact of the sulfide solution with the contaminant occurs when the waste is continually mixed.

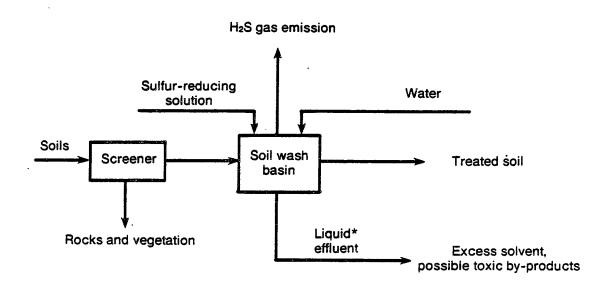
3.3.1.2 Applicability.

- (a) This process is used commercially for metals removal from aqueous waste streams.
- (b) Explosives will be reduced to nonexplosive compounds.
- (c) In-situ treatment could result in migration and contamination of groundwater by the toxic aromatic amines.
- (d) Metallic sulfides will remain in the soil, presenting the potential for contamination on a long-term basis.
- (e) Equipment is available for the on-site reduction process.
- (f) Reactions with sulfur-based compounds and soil have not been reported.
- (g) This process is more suitable for decontaminating soils containing only explosives and organics without the presence of heavy metals.

TNT Na₂S
$$NH_2$$
 NH_2 $NH_$

Source: Benecke et al., 1983

a. Sulfur reduction of explosives — reaction products.



- b. On-site sulfur reduction process flow diagram.
- * Contains toxic compounds that may require further treatment.

Figure 19. Sulfur-based reduction.



3.3.1.3 Comments.

- (a) Toxic products are formed from nitro aromatics (e.g., TNT, DNT) and nitramine explosives (e.g., HMX, RDX).
- (b) Sulfur-based reductants produce hydrogen sulfide gas as a by-product. However, this may be minimized by maintaining alkaline conditions in the reaction area.

3.3.1.4 References.

- (a) Benecke et al., 1983.
- (b) Coia et al., 1983.
- (c) EPA, "Technology for the Metal Finishing Industry," 1980.
- (d) Alexander, 1965.



- 3.3.2 Chemical reduction with sodium borohydride (NaBH₄).
- 3.3.2.1 Description. Sodium borohydride is a reagent used in the reduction of organics such as aldehydes, ketones, and alcohols, along with inorganic metallic compounds. The contaminated medium and a sodium borohydride solution are mixed in a vessel, as shown Figure 20. The contaminated medium should be agitated or mixed to ensure optimal contact. Residence times of 15 to 30 minutes have been reported for contaminated solutions. The solutions will reduce explosives to nonexplosive products as shown below:

$$R_2$$
 NNO₂ (RDX, HMX) $\xrightarrow{N_aBH_4}$ R_2 NNH₂

2,4,6-TNT, N_aBH_4 Aromatic amines based solvents
2,4-DNT, $\xrightarrow{}$ or derivatives tetryl Cobalt salt

Metals can be recovered via precipitation using sodium borohydride as the reducing agent. The waste stream is mixed with the borohydride at a pH between 8 and 11. The metals are reduced to their pure form (in aqueous solutions the metals would be precipitated and recovered using conventional unit processes).

This process may be applied in-situ by "flooding" a contaminated site with sodium borohydride solution. However, complete reactivity is not ensured with this method; there would also be the possibility of contaminating the groundwater.

- 3.3.2.2 Applicability.
- (a) This process is used commercially for metals removal from aqueous waste streams.
- (b) Explosives will be reduced to nonexplosive compounds.
- (c) Adaptable equipment is available for on-site reduction.
- (d) Reduction with sodium borohydride and soil has not been reported either in-situ or on-site.
- 3.3.2.3 Comments.
- (a) The liquid effluent from this treatment process is likely to contain hazardous aromatic amines that require further treatment before discharge.



(b) Solid NaBH₄ should be handled according to accepted safe practices for flammable hygroscopic powders.

(c) Any reduction reaction involving NaBH4 may cause the evolution of hydrogen gas, creating a potentially explosive atmosphere.

3. 3. 2. 4 References.

- (a) Benecke et al., 1983.
- (b) Jula, 1974.
- (c) Sodium borohydride, Thiokol/Ventron Division, 1979.

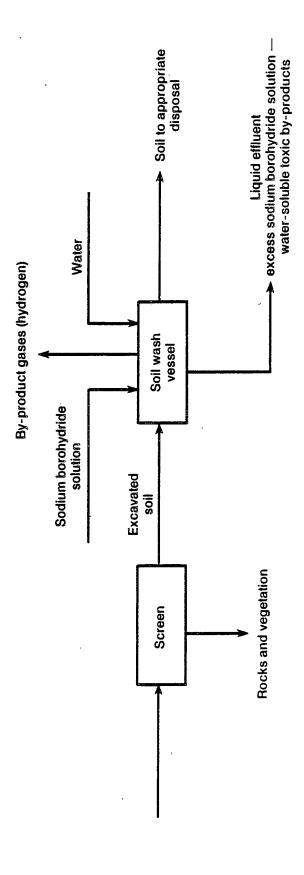


Figure 20. Sodium borohydride reduction — process flow diagram.



3.3.3 Solvent extraction (on-site).

3.3.3.1 Description. Solvent extraction or leaching of waste streams is the process of separating soluble organic or inorganic compounds by bringing the contaminants into contact with an appropriate solvent. Contaminated wastes will be placed in an extraction vessel and then washed with the appropriate solvent. This process is shown on Figure 21. The solvent should be chosen based on its ability to desorb the contaminant from the waste, and the ease of separating the solvent from the adsorbed contaminant.

After washing the soil, it is dried, and can possibly be returned to the site. The solvent is recovered using typical liquid recovery processes, such as, distillation, while the contaminant is concentrated in any remaining solvent. The concentrated solvent is then destroyed on-site or may be further processed. This process can be designed to recover most contaminants.

3.3.3.2 Applicability.

- (a) Solvent extraction of explosives from soils has been successfully demonstrated in laboratory studies by Atlantic Research.
- (b) Most explosives can be extracted using acetone.
- (c) Metals can be extracted using acids (demonstrated industrial processes).
- (d) Metals have been recovered from ores using ammonia.
- (e) A soil with a contaminant profile including heavy metals and explosives could be difficult to decontaminate using one solvent.
- (f) Solvents that have been successful in extracting explosives are usually flammable.
- (g) Solvents that desorb metals tend to form hazardous or explosive by products.
- (h) Equipment exists to perform solvent extraction on-site.
- (i) Systems for PCB decontamination of soils have been designed to be mobile (e.g., Acurex, Suntech, EPA).

3.3.3.3 Comments.

- (a) Solvent extraction produces a concentrated waste stream that must be treated.
- (b) An example of a commercial process for nickel recovery from sulfide ores is shown on Figure 22.



3.3.3.4 References.

- (a) Beaudet et al., 1983.
- (b) Wentsel et al., 1981.
- (c) Shuckrow et al., 1980.
- (d) Jones et al, 1981.
- (e) Personal communication with D. B. Chan, Navy Construction Engineering Laboratory, 13 June 1983.

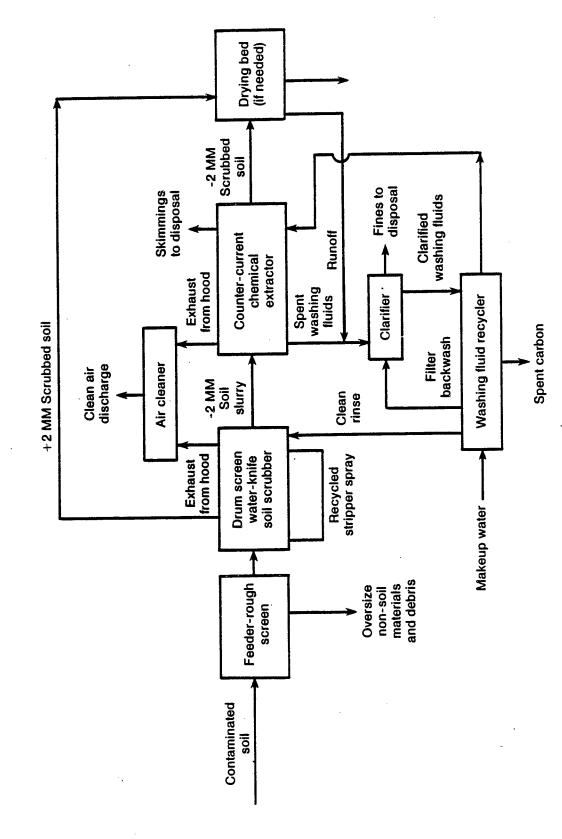


Figure 21. Typical on-site solvent extraction process for soils.

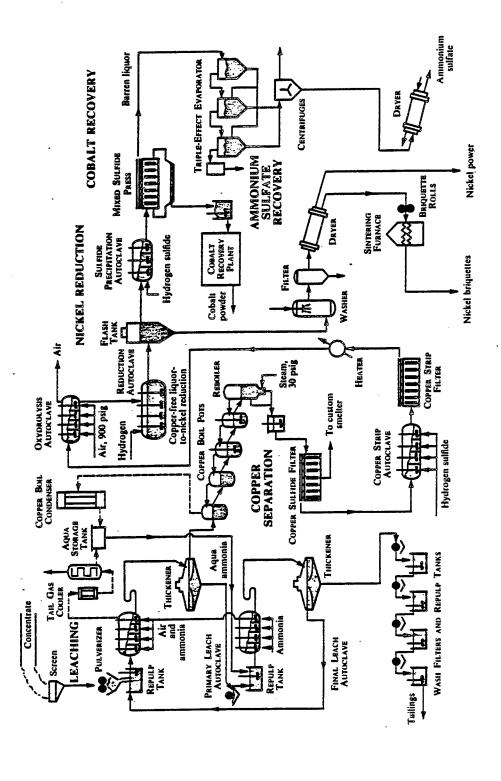


Figure 22. Nickel recovery from sulfide ores.



- 3.3.4 Solvent extraction using the Acurex process.
- 3.3.4.1 Description. Organics-contaminated soil is excavated and placed into modular soil-washing vessels, as illustrated on Figures 23 and 24. The soil is washed with an organic solvent that is made up of several blended compounds and is considered proprietary by Acurex. The contaminated solvent is then removed via vacuum extraction and is transferred to the solvent recovery area. The soil is dried and placed in a suitable location.

The contaminated solvent is fed to a column where the solvent is reclaimed. Contaminants are concentrated at the bottoms of the recovery columns and sent to a reactor vessel. In this vessel the Acurex reagent (proprietary) is added that reacts with the toxic material forming a nontoxic sludge that must be disposed of.

3.3.4.2 Applicability.

- (a) The system is not available commercially, but has been tested in the field by EPA. Acurex hopes to have a demonstration by May 1984, and is currently seeking funding for such a project.
- (b) The system was developed to remove chlorinated organics from soils (e.g., PCB's).
- (c) There is no reported experience with removing explosive compounds from soils.
- (d) The system has been developed to be mobile.
- (e) The effect that metals have on the efficiency of this process is unknown at this time.

3. 3. 4. 3 Comments.

- (a) The sludge stream generated requires disposal.
- (b) Residual solvent may be adsorbed by soil.
- (c) Cleanup cost estimate: \$200 to \$500/cubic yard (June 1983).

3.3.4.4 References.

- (a) Piasecki, 1983.
- (b) Personal communication with Leo Weitzman on 15 June 1983 and 30 August 1983.
- (c) Vendor information from Acurex, Inc., Cincinnati, Ohio.

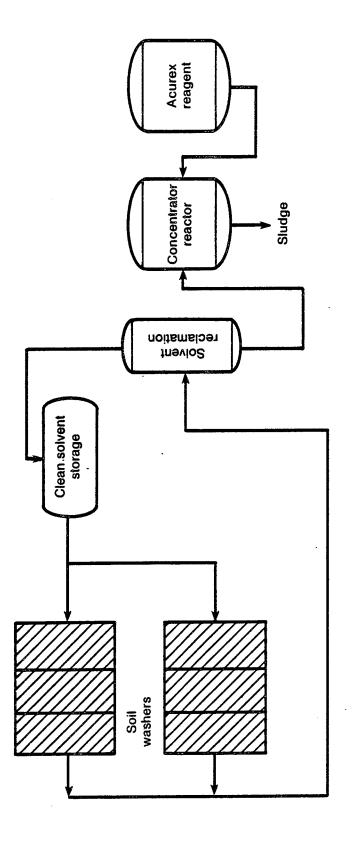


Figure 23. Acurex process — process flow diagram.

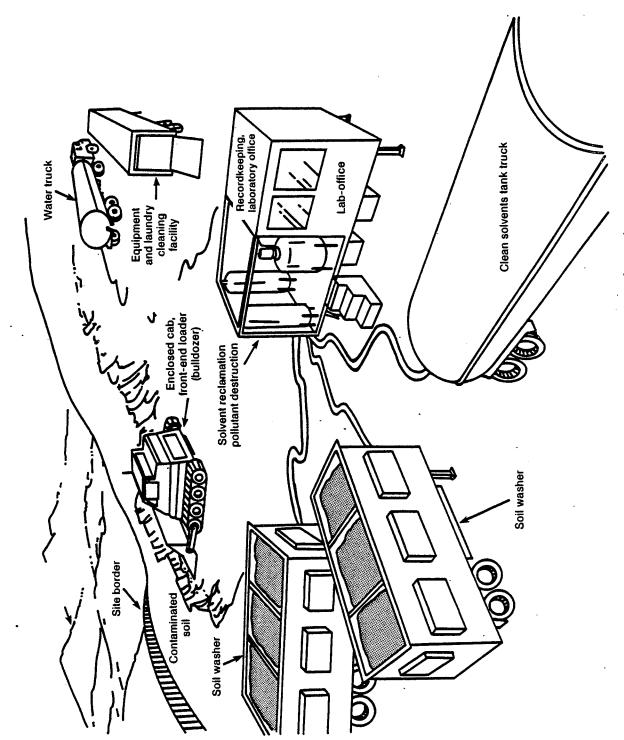


Figure 24. Typical site cleanup equipment.

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3.3.5 Solvent extraction (in-situ).

3.3.5.1 Description. Solvent extraction in-situ (Figure 25) relies on the same chemical and physical properties as on-site solvent extraction. The difference is that the contaminated soil is not removed from its original site -- it is treated in place. For successful solvent extraction the contamination zone must be defined and possibly isolated using any containment technology. Injection and vacuum wells are then located on the contaminated site based on the area's geography and geological structure.

The selected solvent is injected into the contaminated site and allowed to leach contaminants from the soil. The solvent is then withdrawn via the vacuum wells and pumped to a solvent recovery unit. Here the contaminants are concentrated and then destroyed or further processed. The recovered solvent is injected back into the contaminated zone for further leaching (extraction) of contaminants.

3.3.5.2 Applicability.

- (a) This process is used for in-situ mining of uranium using sulfuric acid as the solvent.
- (b) EPA has used this process to recover water-soluble contaminants.
- (c) Different soil types may hinder solvent contact with the soil.
- (d) This process is difficult to control (solvent may channel through soils).
- (e) The system can be designed to be mobile.
- (f) This unit process can easily be integrated with other processes to form a successful treatment system.

3.3.5.3 Comments.

- (a) Solvents needed to successfully decontaminate soil may cause groundwater contamination.
- (b) A list of explosive solubilities in different solvents appears in Appendix B.

3.3.5.4 References.

- (a) Beaudet et al., 1983.
- (b) Wentsel et al., 1981.
- (c) Shuckrow et al., 1980.
- (d) Jones et al., 1981.
- (e) Kubarewicz et al., 1983.
- (f) Personal communication with D. B. Chan, Navy Civil Engineering Laboratory, 13 June 1983.

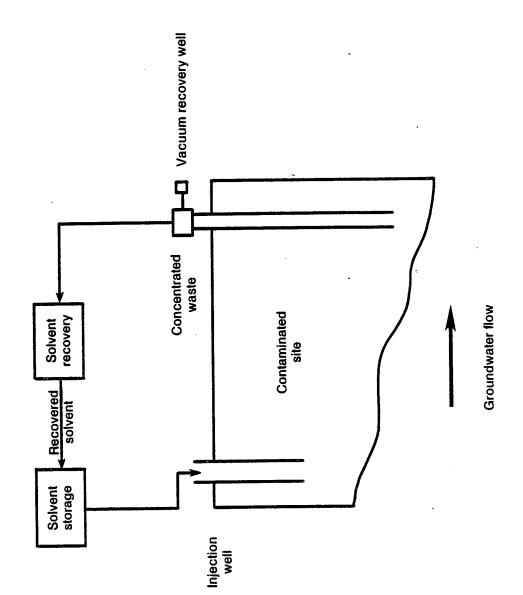


Figure 25. In-situ solvent extraction — process schematic.

1 ..



- 3.3.6 Decontamination of soils using Franklin solvent.
- 3.3.6.1 Description. The Franklin solvent is a proprietary compound that is believed to be a sodium polyethylene glycol mixture. This compound reacts with toxic chlorinated organic compounds to form nontoxic products (the chlorides will react with the sodium, forming a salt). This solvent is applied directly to contaminated soils and allowed to react in-situ. No further treatment would be necessary, as the reaction products and solvent are biodegradable and nontoxic.

3.3.6.2 Applicability.

- (a) This process has been demonstrated in the laboratory to dechlorinate polychlorinated biphenyls (PCB's).
- (b) This process is scheduled for in-situ field testing in Buffalo, New York beginning on 23 August 1983 by EPA research.
- (c) There are no published reports on the solvent's effect on explosives or heavy metals.
- (d) There are possible side reactions that could form phenyls or biphenyls.

3.3.6.3 Comments.

- (a) Products of in-situ treatment are NaCl and other nontoxic glycolic organics (exact composition is unknown). The organics should be very susceptible to natural biodegradation.
- (b) This system has the potential to be extremely cost-effective.
- (c) Groundwater contamination may occur from in-situ treatment as a result of the increased mobility of hazardous compounds.

3.3.6.4 References.

- (a) Beaudet et al., 1983.
- (b) Personal communication with Charles Rodgers, EPA-IERL, 7 June 1983.



- 3.3.7 Free radical oxidation.
- 3.3.7.1 Description. Oxidation removes organic contaminants by utilizing a free radical mechanism that can decompose even refractory explosive compounds.

Molecules are first excited to break bonds and produce free radicals. Excitation may be thermal, catalytic (i.e., Fenton's reagent), or photochemical; thermal methods are considered prohibitively costly. Waste is usually treated in an aqueous or slurry state to take advantage of the H⁺ and OH⁻ radicals that are produced by water. These will form ozone and hydrogen peroxide, O₃ and H₂O₂, both powerful oxidants. Other oxidants are produced by the excited organic compounds, or oxidants can be supplied to the system. Figure 26 indicates the mechanism of decomposition.

Oxidation is used commercially to treat sludge, and laboratory studies have investigated the feasibility of oxidation for explosive contaminants. Methods of effecting oxidation include the following:

- (a) UV/ozone treatment.
- (b) Gamma irradiation.
- (c) Electron beam treatment.
- (d) Ultrasonic treatment.
- 3.3.7.2 UV/ozone.

<u>Description</u> - Ultraviolet radiation enhances the oxidizing power of ozone by 100 to 10,000 times, and is effective for the oxidation of refractory compounds such as explosives and metallic compounds.

Ozone is produced from either air or oxygen. It must be generated on-site due to its rapid decomposition (half-life of about 20 minutes). Ozone will also autodecompose if too much UV is used. Peroxides may be substituted for ozone, but they are less effective. Chlorates should not be used as oxidants in this case because of the problems associated with chlorinated hydrocarbons.

The usual reactor for UV treatment is a multistaged continuous stirred tank reactor (CSTR). Ultraviolet rays have poor penetrating ability, and this type of reactor maximizes the mass transfer to the liquid waste from the gaseous ozone.

1. Excitation of molecules to produce free radical R*.

3. Addition of ozone and release of oxygen molecule.

5. Product of step 4 is unstable and will rearrange immediately.

6. Oxidation continues until a one-carbon chain produces CO₂ and water.

Figure 26. Mechanism for free radical oxidation. (Example for carboxylic acid, as given by Prengle et al., 1975.)

Applicability -

(a) UV treatment is currently used to disinfect wastewater sludges, and has proven effective for handling refractory and toxic compounds. Operating costs are relatively high. This process is best suited for dilute aqueous wastes because of the poor penetrating ability of the rays.

(b) RDX and TNT in the ppm range (aqueous phase) have been removed with UV treatment in less than 2 hours (Jones et al., 1981). However, no data are available for

higher concentrations.

(c) Andrews is reported to have obtained complete decomposition of aqueous TNT at 100 ppm in 1 percent acetone. Ring cleavage occurred, and the products were CO₂, NH₃, and a small amount of cyanide (Benecke et al., 1983).

(d) No testing on contaminated soil has been reported.

(e) This system should remove organic solvents from the aqueous phase; no soil testing for solvents has been reported.

3.3.7.3 Gamma irradiation.

Description - Liquid or dried waste is conveyed around a source of gamma irradiation, such as cesium-137 or cobalt-60. Gamma rays penetrate more deeply than UV rays or electron beams, so bulkier wastes can be treated. The process should be shielded to prevent any unnecessary scattering of rays.

The degree of degradation is determined by the exposure time; complete degradation can be achieved. Organics decompose to volatile compounds of disputed toxicity.

Applicability -

(a) This process has recently been implemented for commercial sludge treatment, following a successful pilot plant operation in New Mexico.

(b) The effect of gamma irradiation on certain explosives (TNT, RDX, and tetryl) was studied by Wentsel et al., 1981. A 30 percent reduction of explosives was reported at a dosage of 4.1 megarads. The researchers concluded that this process was economically unfeasible for treating wastes with high explosives concentrations, although it might be a worthwhile alternative for lower concentrations.



(c) These findings are based on explosives in wet sediments, but decomposition of wet sediment may be explosive (Benecke et al., 1983). Gamma irradiation of dry TNT and RDX was reported to be a much slower process. Wentsel et al. found little decomposition of dry TNT even when subjected to 20 megarads.

3.3.7.4 Electron beam.

Description - High energy electrons (beta particles) are used to bombard the waste to stimulate the formation of free radicals. A beta particle has poor penetrating ability, only slightly superior to a UV photon. There is a potential hazard posed by x-rays resulting from collisions between nuclei and electrons. This problem can be avoided by operating below a threshold voltage of 10 MeV.

Applicability -

- (a) This is not a widely used technology. A pilot plant was operated by the Massachusetts Institute of Technology (MIT), but plans for a commercial installation in Florida have been shelved. The pilot plant used electron beams for liquid sludge disinfection and was able to reduce pathogens to undetectable levels.
- (b) An electron beam facility would have a high construction cost, but operating costs would be low.
- (c) No testing on explosives or solvents has been reported.

3.3.7.5 Ultrasonic treatment.

Description - Ultrasonic cleaning is a surface scrubbing technique that consists of an ultrasonic generator, a transducer, a cleaning tank, a liquid couplant/solvent, and a heater. The generator converts line power from 60 Hz to a higher frequency (18 to 90 kHz). The transducer converts these high-frequency impulses to low-amplitude mechanical energy of the same frequency. The warm liquid couplant (150 to 170°F) transmits this energy to the material to be cleaned. The compression-rarefaction-compression wave cycle transmitted by the generator causes the liquid to cavitate and implode, creating minute quantities of energy with tremendous localized force. Pressure and temperatures are approximately 10⁴ psi and 10⁴⁰C, respectively. Localized high temperatures may cause decomposition of some explosives (Benecke et al., 1983). The liquid couplant will become contaminated and must be further treated.



Applicability -

- Ultrasonic cleaning is used commercially in the elec-(a) tronics industry.
- This technology has also been applied to the surface (b) cleaning of nuclear equipment.
- Research with explosives reported 99 percent TNT de-(C) struction after 1 hour with ultrasound-catalyzed ozone oxidation of an aqueous system (Sierka, 1982).
- effectiveness of this process is as a surface re-(d) moval technique, and it is possible that the couplant may only carry the contaminant deeper into porous materials. Feasibility would depend on the cost of electric power and the efficiency of its use.

3.3.7.6 References.

- UV/ozone. (a)
 - Benecke et al., 1983.

 - Prengle et al., 1975.
 Weston, Roy F., Inc., "Cost Estimating Guide for Municipal Wastewater Treatment."
 - Guarino et al., 1981.
 - Baer, 1979.
 - Paulson, 1977.
- Gamma irradiation.
 - Beaudet et al., 1983.
 - Benecke et al., 1983.

 - Wentsel et al., 1981. Weston, Roy F., Inc., "Cost Estimating Guide for Municipal Wastewater Treatment."
- Electron beam. (C)
 - Beaudet et al., 1983.
 - Weston, Roy F., Inc., "Cost Estimating Guide for Municipal Wastewater Treatment."
- Ultrasonic treatment. (d)
 - Benecke et al., 1983.
 - Sierka, 1982.



- 3.3.8 Free radical oxidation (Enercol oxidation process).
- 3.3.8.1 Description. This process involves free radical oxidation of organic compounds using ultraviolet light and cavitation to generate free radicals (see Figure 27). Hydrogen peroxide is used as the oxidizing agent for this process. The solid or aqueous waste stream is fed into a vessel where it comes in contact with the peroxide solution. This stream is then fed into a vessel where cavitation is produced hydraulically using a patented nozzle design. The forces produced during cavitation rupture the organic bonds of the waste stream, preparing the stream for the free radical oxidation.

This stream is preheated and fed into a series of reactors. In the reactors ultraviolet light is fed at specific wave lengths to further excite the organic molecules. Hydrogen peroxide, fed in low concentrations into the reactors, is split into two hydroxyl radicals under reaction conditions (temperatures are at the boiling point of the waste stream at pressures of 20 to 60 psig). When combined with a catalyst (considered proprietary), the initiation and maintenance of the free radical reaction is enhanced.

The total time for the completion of the oxidation reaction is estimated by Enercol to be 15 minutes. The system uses the heat generated in the oxidation reaction to preheat the feed into the reactors. Settling equipment may be required to recover inorganic products that enter this system.

3.3.8.2 Applicability.

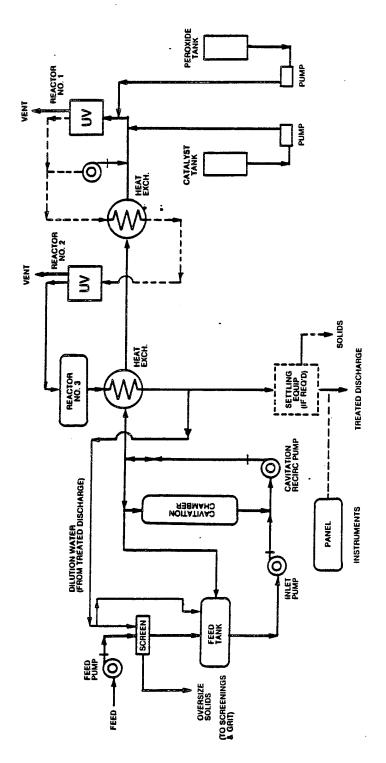
- (a) The Enercol process was commercially available in 1982, but the vendor is no longer marketing it.
- (b) A wide range of organics can be oxidized, according to vendor-published reports. Data are unavailable for the treatment of any specific compounds.
- (c) This system does not remove inorganics or heavy metals. The presence of these contaminants should not affect the operation of this process.
- (d) The Enercol system can treat slurries (sludges) or aqueous streams.
- (e) The adaptability to soils is unproven at this time.

3.3.8.3 Comments.

(a) This process produces solid wastes of unknown toxicity that must be disposed of.



- 3.3.8.4 References.
- (a) Enercol, Inc., "Treatment of Industrial Wastes and Sludges," Technical Bulletin No. 100, 1981.



Source: Vendor information, Enercol, Inc.

Figure 27. Enercol oxidation process - process flow diagram.



3.3.9 Fenton's reagent.

3.3.9.1 Description. This process uses a chemical solution to catalyze the free radical oxidation of many organic compounds. Fenton's reagent is a slightly acidic solution of ferrous salts in aqueous hydrogen peroxide. This reagent provides hydroxyl radicals, as follows:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH$$

The hydroxyl radical initiates the decomposition of many organics compounds, including the explosives TNT, DNT, RDX, and HMX. A free radical mechanism produces unstable intermediate decomposition products, which further decay into nontoxic gaseous compounds, such as CO_2 , NO_3 , and N_2 .

3.3.9.2 Applicability.

- (a) All data are from laboratory-scale work. The suitability of Fenton's reagent for the treatment of explosives-laden lagoon sediments is currently being investigated by Engineering Science for USATHAMA.
- (b) Fenton's reagent is an inexpensive and safe chemical.
- (c) Fenton's reagent is best suited for on-site treatment of excavated soil. There is no need to first extract contaminants from the soil, however. In-situ treatment has been suggested, but there is a problem with iron entering the groundwater. A flow diagram for on-site treatment is shown on Figure 28.

3.3.9.3 Comments.

- (a) Explosives are not soluble in the aqueous reagent. A surfactant or complexing agent would be necessary to solubilize the contaminants.
- (b) If DMSO (dimethylsulfoxide) is used as a cosolvent, methyl radicals will be produced. Methyl radicals are even more reactive than hydroxyl radicals.

3.3.9.4 References.

- (a) Benecke et al., 1983.
- (b) Kubarewicz et al., 1983.

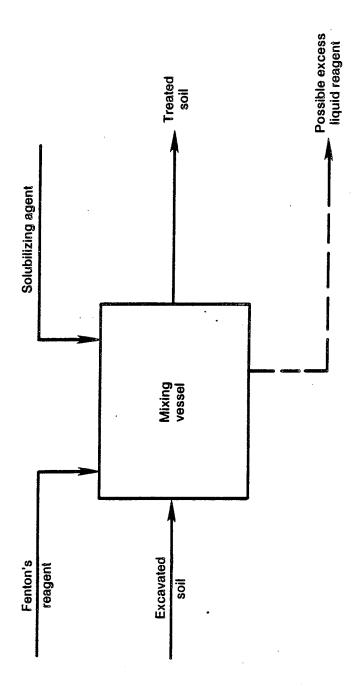


Figure 28. Fenton's reagent.



- 3.3.10 Base-initiated decomposition (alkaline hydrolysis).
- 3.3.10.1 Description. Basic solutions (pH around 10) have been shown to initiate free radical decomposition of certain organic explosives. Basic solutions furnish hydroxyl radicals that initiate the conversion to unstable intermediates. These compounds rapidly decompose to form volatile gases and nontoxic products of low molecular weight.

3.3.10.2 Applicability.

- (a) This process is easily adaptable to in-situ treatment if the proper basic solution is used. On-site treatment avoids the risk of contaminating the soil or groundwater with excess base. The process diagram for on-site treatment is shown on Figure 29.
- (b) Data for TNT decomposition are incomplete, but preliminary studies have indicated that TNT decomposition products are similar to DNT products.
- (c) Explosives that have been shown to decompose in basic solutions include: RDX, HMX, DNT, NC, and lead azide. Figure 30 shows the decomposition products of these explosives.
- (d) In-situ base-initiated decomposition of explosives in lagoon sediments is being investigated by ESI for USATHAMA.

3.3.10.3 Comments.

- (a) Surfactants or complexing agents may be necessary to improve the solubility of explosives in basic solutions. Ammonium halide surfactants have proven effective with RDX, HMX and NC, but cannot be used with TNT due to the formation of insoluble products. These surfactants have been found to have a catalytic effect on decomposition as well.
- (b) The process will not solubilize the heavy metal contaminants that are present in the soil.
- (c) One decontamination solution that may prove applicable to explosives decomposition is DS2, a solvent containing sodium hydroxide. DS2 has been used to decompose nerve gases; its suitability for explosives is based on the high solubility of the organics in DS2. DS2 poses some operational hazards because it is a skin irritant and a flammable compound.

3.3.10.4 References.

(a) Benecke et al., 1983.

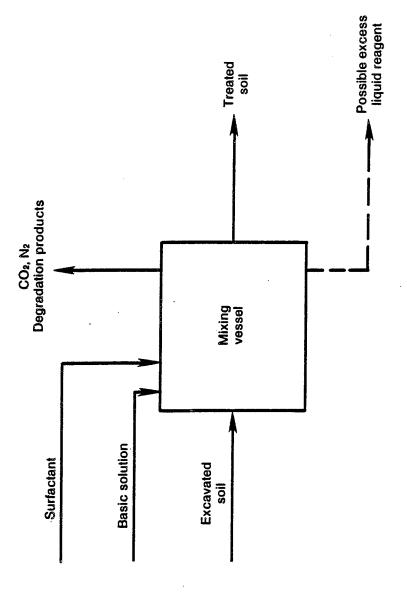


Figure 29. Base-initiated decomposition.

RDX, HMX OH- mic. cat. (anion) fast CH₂O, N₂O, NH₃, N₂, HCO₂-

NG OH CH3CO2, HCO2, NO3, NO2

NC OH org. acids, NO₃, NO₂, NO_X, CO_X, cyanides

NQ OH N2O, CO2, NH3

ArNO₂(TNT,DNT) OH^- ArOH Pb(N₃)₂ OH^- Pb(OH)₂ + N₃

Hazardous products

RDX, HMX: CH₂O, N₂O, NH₃

NG: none

NC: NO_X, CO_X, cyanides

NQ: N₂O, NH₃

Lead azide: Lead hydroxide

Source: Benecke et al., 1983

Figure 30. Reactions for base-initiated decomposition of explosives.



3.3.11 Carbon adsorption.

3.3.11.1 Description. Activated carbon is a solid adsorbent that removes organic compounds from a contacting liquid by accumulating them on the carbon surface. The porous solid provides a surface area of 500 to 1,500 square meters/gram of adsorbent.

Adsorption can be either a batch or a continuous process. Batch reactors, using powdered carbon, have contact times between 20 to 60 minutes. Larger amounts of organics are removed using multistage reactors.

The continuous processes most commonly used (Figure 31) are either downflow or upflow fixed beds, although fluidized beds are occasionally used. Granular activated carbon is packed 3 to 9 meters high in the column, with a contact time of 10 to 60 minutes. Swing adsorbers are usually used to allow regeneration of one bed without interruption of the liquid flow. Activated carbon is thermally regenerated at temperatures of 800 to 950°C. Reactivation of carbon at these temperatures is by oxidation with steam, ∞ , or 0_2 .

3.3.11.2 Applicability.

- (a) Activated carbon technology is established and widely used for water purification. Water odor and color are decreased by removing nonbiodegradable organics.
- (b) The process is known to effectively remove TNT from aqueous solutions. No data are available for the removal of TNT from soil extracts.
- (c) Adsorption is used commercially for explosives removal but its major drawback is the prohibitive cost of fresh activated carbon. Carbon with adsorbed TNT cannot be thermally regenerated because toxic fumes would be released, thus it must be disposed of. Chemical regeneration is ineffective in this case.
- (d) Carbon adsorption is practical only for liquid wastes.
 A soil slurry would clog the carbon, leading to rapid deactivation.

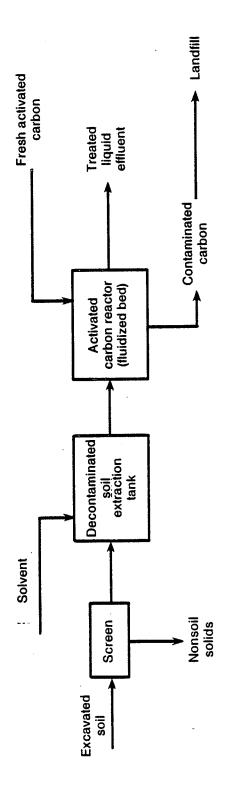


Figure 31. Carbon adsorption.



3.3.11.3 Comments.

- (a) Adsorption is not specific for any compound. The presence of other organics may hinder the adsorption of the compounds of interest. This poses a problem if an organic solvent, such as acetone, is used to extract contaminants from the soil.
- (b) Activated carbon treatment is often used in conjunction with aerobic degradation. Zimpro's PACTR process uses powdered carbon to provide a surface area for microorganisms, which later serve as nuclei for bacterial floc settling. The carbon regeneration is less frequent, as the carbon adsorbs only those compounds that are refractory to microbial degradation.

3.3.11.4 References.

- (a) "Treatment and Disposal of Industrial Wastewaters and Residues," Proceedings from national conference, 1977.
- (b) Sundstrom and Klei, 1975.
- (c) Lanouette, 1977.
- (d) Conway, 1980.
- (e) Shuckrow, 1980.
- (f) Shapira et al., 1977.



3.3.12 Ion exchange.

3.3.12.1 Description. Metallic ions are removed from a contacting solution by exchange with free ions of a resin. Ion-exchange resins are solid matrices with bound ions of one charge and loosely-held ions with the opposite charge. Exchange continues until all of the resin-free ions have been displaced. The process flow diagram is shown on Figure 32.

If valuable, the captured ions are recovered. The resin is chemically regenerated with an excess solution of the original ion.

Fixed beds are used for ion exchange. Operation can be cyclical, with in-place regeneration of the resin, or continuous. Industrial applications utilize the latter, circulating the resin to another vessel for regeneration. Few resins are ion-specific, and most will remove ions of a similar size and charge. Mixed beds have anion and cation exchange resins intermixed.

3.3.12.2 Applicability.

This process is an established technology for industri-(a) al metals recovery. It is also widely used for water purification and demineralization.

Ion exchange is best suited for small volumes; larger (b) volumes are more economically treated by chemical

precipitation.

Resins have a constant stoichiometric exchange capacity (C) and cannot handle higher concentrations efficiently. Above 600 ppm of dissolved solids, multistaging or recycling is necessary.

In-situ application of resins in soils is possible, es-(d) pecially to protect groundwater. Contaminants would have to be first desorbed from the soil for in-situ

treatment.

Organic compounds can foul the exchange resin and (e) substantially impair the effectiveness of the metals removal.

3.3.12.3 Comments.

Contaminants would have to first be extracted from the (a) soil because the ion exchange process only operates with a liquid feed.

The contaminated regenerant solution must be further (d)

treated or disposed of.



3.3.12.4 References.

- Sundstrom and Klei, 1975. (a)
- "How the Cation Exchange Works," 1977. (b)
- (C)
- Perry, 1963. Lanouette, 1977. (d)
- Shuckrow et al., 1980. (e)

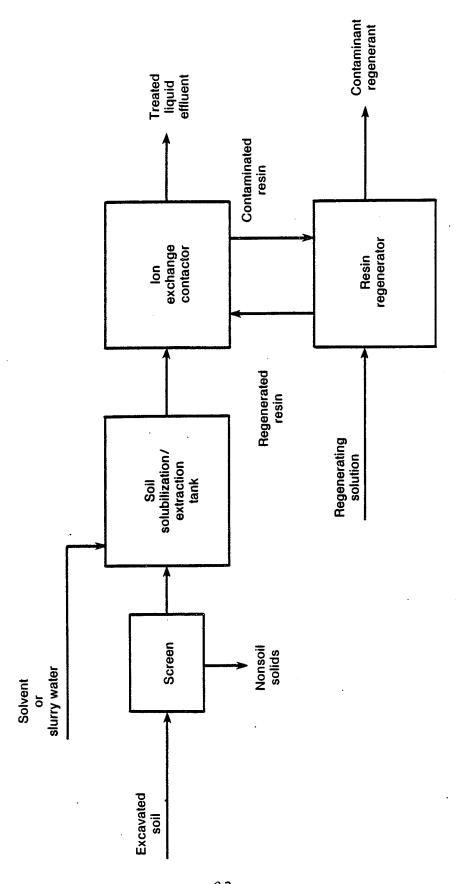


Figure 32. Ion exchange.



3.3.13 Surfactant complexing.

3.3.13.1 Description. Recent studies have indicated that certain amino surfactants under alkaline conditions rapidly complex TNT and other explosive-related organics to form water-insoluble, nonexplosive precipitates.

This process may be performed in-situ at a contaminated site. The selected surfactant is injected into the contaminated site. This solution will react with TNT forming TNT-surfactant complexes. These complexes are insoluble in water, and thus leaching into the groundwater should not occur. It is hoped that these complexes would then be more easily biodegraded.

The solid product resulting from the surfactant complexing process for aqueous explosives is a nonexplosive, dark brown tar that can be dried and burned safely.

Surfactant complexing technology developed from research in foam separation techniques. In this process a gas (usually air) is bubbled through a liquid to produce a foam. Surface-active substances accumulate at the interfacial surfaces furnished by the foam, which is then removed from the liquid.

Foam separation has been studied for organic compounds such as phenol alkyl benzene sulfates, enzymes, and naphthalene derivatives. Most of these must be treated to become surface active. Metallic ions can be removed from aqueous waste streams by using chelating surfactants to complex with the metal ions at the interfacial surface.

3.3.13.2 Applicability.

- (a) The process has been tested in the laboratory using Duoquad T-50, in a basic solution, as the surfactant. Studies indicated that in-situ immobilization of TNT in soils would require large quantities of surfactant in solution (30 to 1 molar ratio surfactant to TNT) (Kaplan, 1982). Mutagenicity studies have indicated that the complexes formed were more potent mutagens than TNT. The surfactant was unable to complex TNT biodegradation compounds that were present in tested soils.
- (b) The surfactant treatment accelerated the hydrolysis of HMX and RDX. In these reactions the surfactant serves as a catalyst for the hydrolysis under alkaline conditions. 2,4-DNT forms an insoluble complex with Duoquad T-50.



(c) Researchers have obtained 99.9 percent TNT removal from aqueous solutions in 6 hours (85 percent removal in 2 hours, 99.5 percent in 4 hours). The initial TNT concentration was 120 to 150 ppm, and three surfactants were tested, one amine, and two fatty diamine compounds (Okamoto et al., 1977). Their findings have not been tested in a larger-scale system, and no other explosives have been tested.

(d) Heavy metals in soils should be unaffected by this treatment. No data for heavy metals have been report-

ed.

3.3.13.3 Comments.

(a) In-situ treatment may lead to contaminated groundwater resulting from excess surfactant or caustic used in the application.

(b) The advantage of surfactant complexing, relative to foam separation, is that the filtration process is a

simpler separation as well as a less costly one.

3.3.13.4 References.

(a) Kubarewicz et al., 1983.

- (b) "Treatment and Disposal of Industrial Wastewaters and Residues," Proceedings of the national conference, 1977.
- (c) Conway et al., 1980.
- (d) Kaplan et al., 1982.



- 3.3.14 Removal of metals and complexes with dithiocarbamate (DTC).
- 3.3.14.1 Description. A metallic waste stream is contacted with a fixed amount of DTC via an in-line mixer or in an agitated vessel; the process diagram is shown on Figure 33. The amount of DTC added is based on the level of contamination of the waste stream. The DTC will effectively precipitate complexed or chelated cationic heavy metals from the slurry. The product is effective over a pH range of 3 to 11. Longer contact times result in increased metals removal. The resultant precipitated sludge can be further processed to recover metals prior to ultimate disposal.
 - 3.3.14.2 Applicability.
 - (a) The chemicals and needed equipment are available commercially.
 - (b) The system is commercially used for metals removal from aqueous streams.
 - (c) The technology has not been tested with soil solutions or slurries. The system will recover metals but has no reported applications to organic compounds. The technology may be effective in removing lead-initiating compounds.
 - (d) Equipment can be adapted for transportable systems.
 - 3.3.14.3 Comments.
 - (a) Liquid effluent will contain nonmetallic contaminants after treatment.
 - (b) Sludge leaving the system is hazardous and will require further treatment, or else the dewatered sludge must be disposed of in a secure landfill.
 - 3.3.14.4 References.
 - (a) Vendor information, Pollution Technology Systems, Inc., Garland, Texas, 1982.

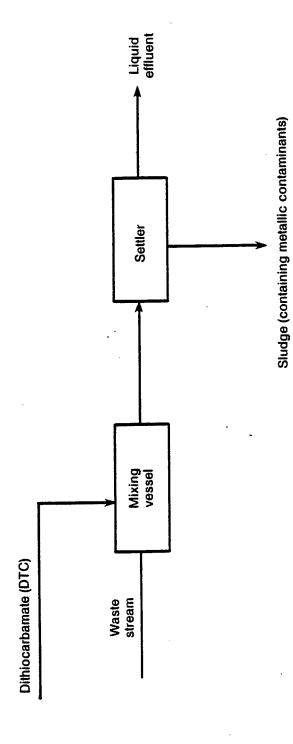


Figure 33. Metals removal using DTC — process flow sheet.



- 3.3.15 Philadelphia Quartz (PQ) process for removing heavy metals.
- 3.3.15.1 Description. Amorphous, hydrated magnesium silicate (Britesorb^R B900) is mixed with a waste stream containing heavy metals (see Figure 34). The slurry of magnesium silicate in the effluent can be heated or pH adjustments can be made to optimize the removal process. The metal ions are complexed by the silicate and effectively removed from the effluent using standard separation techniques. Large amounts of the complexed metal can be recovered using acid extraction. Tests have shown that increased temperature and a 5 percent dosage of magnesium silicate produce optimum results in 30 to 60 minutes.

3.3.15.2 Applicability.

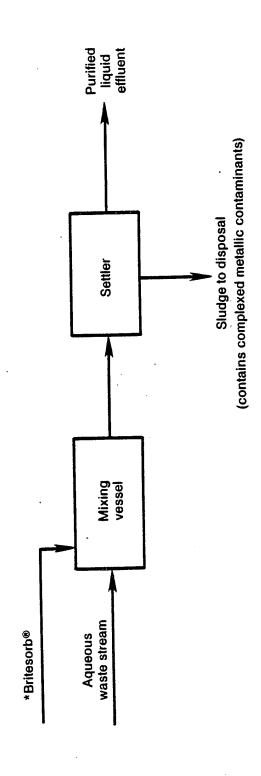
- (a) This system has not been put into commercial use, but it has been demonstrated in the laboratory.
- (b) The system has only been tested on aqueous solutions.
- (c) Organic explosives are unaffected by this treatment method, but do not appear to interfere with the efficiency of the metals removal.
- (d) Metal desorption from soils is likely to be difficult.
- (e) The complexed metallic products will probably be considered toxic and will need to be disposed of.
- (f) This technology may be effective in complexing lead-initiating compounds.

3.3.15.3 Comments.

- (a) Sludge may contain hazardous products that will require additional treatment.
- (b) Soil backfill will be necessary to reclaim a contaminated site.

3.3.15.4 References.

- (a) Patent No. 4,200,527.
- (b) Patent No. 4,200,528.



3

*Amorphous hydrated magnesium silicate.

Figure 34. PQ process for heavy metals removal — process flow diagram.

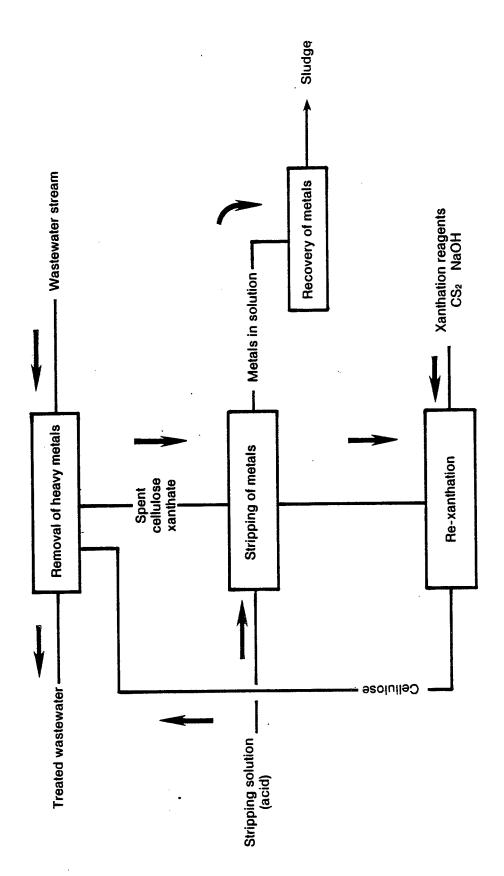


- 3.3.16 Removal of heavy metals using cellulose xanthate.
- 3.3.16.1 Description. Metals-contaminated soil is slurried and transferred to a contacting area where cellulose xanthate is added (see Figure 35). Contact times of 30 minutes under ambient conditions have been shown to produce acceptable effluent quality. A pH between 7 and 9 will ensure consistent results. Temperature was found to have little effect on the complexing of the heavy metals.

The cellulose xanthate-metal complex is very insoluble in the aqueous phase. The complex can be further processed to recover the stripped metals using an acid solution. Cellulose, a product from the stripping operation, can be re-xanthized and returned to the metals removal vessel.

This process may be performed in-situ by flooding a contaminated site with a cellulose xanthate solution. The solution will react with the metals forming the insoluble metallic complex. This renders the metals immobile in the soil.

- 3.3.16.2 Applicability.
- (a) This technology has been demonstrated in the laboratory with aqueous waste streams (Hanway et al., 1976). No work with slurries or soils has been reported.
- (b) The process has not been demonstrated to remove or desensitize organic contaminants in solution, slurry, or soils.
- 3.3.16.3 Comments.
- (a) Aqueous stream treatment produces a residual sludge that may be hazardous because of the metals that are concentrated in it.
- (b) This process developed from starch xanthate treatment, which produces a less manageable sludge.
- (c) The pH of the sludge produced by this treatment often must be adjusted with lime or caustic to raise it to an acceptable discharge value.
- 3.3.16.4 References.
- (a) Hanway et al., 1976.



Source: Hanway et al., 1976

Figure 35. Flow sheet of cellulose xanthate process for heavy metals removal.



3.4 Biological processes.

- 3.4.1 Microbial bioaccumulation of metals.
- 3.4.1.1 Description. Natural or mutant microorganisms are mixed in with a metal-containing aqueous waste. The microbes selectively accumulate the metals in their bodies. These microbes are subsequently separated from the waste solution as biomass, and the concentrated elemental metals are recovered by burning the microbes.

A variation of this technology is microbial leaching; the prime application is the removal of copper from sulfide ore. A microorganism converts the copper into a water-soluble form, which is then extracted from the solution.

3.4.1.2 Applicability.

- (a) Microbes are known for the bioaccumulation of cadmium, copper, iron, lead, molybdenum, radium, and uranium.
- (b) Polybac and the O'Kelley Company are studying the use of microbes for metals removal from wet-scrubber blowdown streams. Research began in August 1982.
- (c) B.C. Research has been the prime investigator of microbial copper leaching. Their 600-gram batch studies have found that 95 percent of the copper is removed, and elemental sulfur has been recovered. B.C. Research has plans to develop their findings in a 2 to 10-tpd pilot system. However, this technology is not expected to be usable within the next 5 to 10 years (Short and Parkinson, Chemical Engineering, 11 July 1983).
- (d) McGill University has patents pending on a number of microbial formulations that recover metals from dilute aqueous streams.

3.4.1.3 Comments.

- (a) The feasibility of separating microbes from soil is unknown; this may impose restrictions on soil decontamination, since a soil slurry or contaminant extract would have to be used.
- (b) If slurrying or extraction is necessary, the desorption characteristics of the soil contaminants would have to be known.
- (c) Metals will have a toxic effect on microbes if they are allowed to reach a certain concentration in their bodies.



3.4.1.4 References.

- (a) Beaudet et al., 1983.
- (b) Short and Parkinson, 1983.
- "Chementator," Chemical Engineering, 23 August 1982. (C)
- (d)
- "New Technology," Chemical Engineering, 11 July 1983. Weston, Roy F., Inc., "The Cost Estimating Guide for (e) Municipal Wastewater Treatment," Currently in draft form.
- (f) Scott, 1978.
- Basta, 1983. (g)
- (h) Personal communication with Dave Watkins, U.S. EPA, Industrial Environmental Research Laboratories.



3.4.2 Immobilized cells.

3.4.2.1 Description. Immobilized cells act as a biological catalyst in specific unit process operations. Cells that are known to metabolize organics are entrapped in a gel or a polymer matrix, which is usually incorporated into a packed bed system. Immobilized cells have been found to metabolize carbon significantly faster than free cells. Fermentation products, such as methane, result from the growth of the cells.

3.4.2.2 Applicability.

- (a) This technique has been used in the pharmaceutical industry to produce stereo-specific amino acids, and in the food industry to produce fructose. Immobilized cells were also studied as a possible means of decolorizing kraft mill effluent (brown color due to lignin).
- (b) This technique has not been tested with contaminated soils or with soil extracts.
- (c) The success of this technique depends on the solubilization of contaminants.

3.4.2.3 Comments.

(a) Fermentation by-products are expected with typical applications of this technology.

3.4.2.4 References.

(a) Vendor information from Polybac Corporation, Allentown, Pennsylvania.



3.4.3 Vermicomposting.

3.4.3.1 Description. Used to implement aerobic biodegradation, vermicomposting uses earthworms in a mesophilic (i.e., ambient temperature of 25°C) composting of organic waste. Vermicomposting is also known as "annelidic treatment."

The burrowing action aerates the soil and mixes the microbes. Microbial activity is enhanced by the presence of the metabolic products released by earthworms. The earthworms also reduce the particle size of the compost, providing more surface area for the bacterial substrate. Vermicomposting is most effective for wastes with a solids content between 30 and 35 percent.

Earthworms will consume their body weight in refuse daily. The treated soil can be returned to use, and the earthworms recovered to be used elsewhere.

3.4.3.2 Applicability.

- (a) This technique has been used successfully for sludge composting in a number of cities, including: Ontario, California; San Jose, California; and Beltsville, Maryland.
- (b) The applicability for explosives degradation using vermicomposting has not been demonstrated.
- (c) Vermicomposting has the same results as aerobic biodegradation, and only serves to catalyze the process.
- (d) There are few data regarding the fate of heavy metals.
 One 28-week study found that cadmium accumulates in earthworm tissue, but other metals (chromium, copper, nickel, lead, silver, and zinc) do not.
- (e) Vermicompost (earthworm castings) is a marketable byproduct of this process. Castings-enriched potting soil is sold nationwide.

3.4.3.3 Comments.

- (a) This technique would have a lower operating cost than composting since no mixing is required. However, vermicomposting operates with a longer residence time and lower surface area to volume ratio than conventional composting. This would indicate that annelidic treatment would have a larger land requirement.
- (b) After vermicomposting, sterilization is necessary if pathogens are present. The soil could also be sterilized by first composting thermophilically.



- (c) Anaerobically-digested sludge is toxic to earthworms.

 This may limit the linkability of vermicomposting and anaerobic degradation.
- 3.4.3.4 References.
- (a) National Conference on Design of Municipal Sludge Compost Facilities, 1978.



3.4.4 Composting.

3.4.4.1 Description. This refers to a controlled biological degradation of the contaminants with other decaying organics, as caused by thermophilic microorganisms (see Figure 36).

Compostable domestic refuse or sludge is prepared (grinding or shredding may be necessary) and mixed with the contaminated soil. The soil is placed into compost piles, and thermophiles are allowed to grow.

Thermophiles liberate neat as they metabolize the organics, and the composting temperature of 60 to 80°C kills most pathogens. Ideally, organic contaminants are mineralized within 90 days; the contaminant-free soil can then be returned to its original site.

Conditions can be maintained to maximize the growth rate. The variables include: carbon to nitrogen (C/N) ratio, moisture content (40 to 60 percent), aeration, and mineral content.

3.4.4.2 Applicability.

- (a) Reported data apply only to TNT; the effectiveness of composting for RDX and DNT has not been demonstrated.
- (b) This technique cannot be used without mineral nutrients; thermophiles will not thrive in unenriched soil.
- (c) Soils contaminated with water-soluble solvents can be accommodated.
- (d) This system will not decompose or remove heavy metals. These metals will hinder organic degradation. Bioaccumulation of metals may kill microbes involved in the degradation process.

3.4.4.3 Comments.

- (a) This technique is very cost effective but can be laborintensive.
- (b) Compost containing explosives must be monitored daily to avoid conditions that may cause an explosion. These conditions are a high pile temperature due to insufficient aeration and mixing, or a low moisture content due to evaporation.
- (c) Possible extensions of this technique include multistaging the piles, and the use of commercial digesters.



(d) The feasibility of this technology depends on the extent of TNT degradation; Osmon and Andrews (1978) reported complete mineralization. Kaplan and Kaplan (1982) disputed this, finding that TNT transformation products resulted. They were difficult to degrade further, and were of unknown toxicity/mutagenicity. The desorption properties of these bioproducts are not known.

3.4.4.4 References.

- (a) National Conference on Design of Municipal Sludge Compost Facilities, 1978.
- (b) Osmon and Andrews, 1978.
- (c) Dallaire, 1978.
- (d) Kaplan and Kaplan, 1982.
- (e) Pavoni et al., 1975.

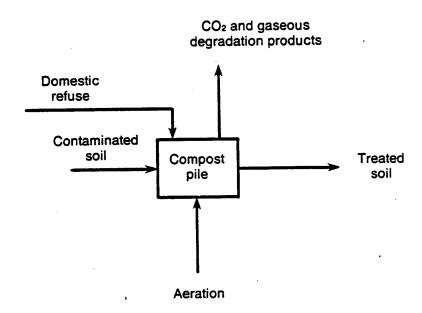


Figure 36. Composting.



3.4.5 Aerobic biodegradation.

3.4.5.1 Description. Microorganisms that consume organic compounds are introduced into the waste. The conditions for their optimal growth are maintained to maximize their consumption of the organic contaminants. If an appropriate culture of microbes can be used, most of the organics can be assimilated. Transformation products of unknown toxicity will result from the degradation of certain explosives.

Aerobic biodegradation can be accomplished in-situ through landfarming. Explosives are not believed to migrate downward through soil at a significant rate; they would be found near the surface.

Other methods of effecting aerobic biodegradation are discussed in subsections 3.4.6 through 3.4.8.

3.4.5.2 Applicability.

- (a) This process is used commercially for wastewater sludge treatment.
- (b) 2,4-DNT and glycerol nitrates degrade readily and completely with this process.
- (c) There are no known aerobes for RDX or 2,6-DNT biodegra-dation.
- (d) All available data are for low explosives concentrations; it is unknown if high concentrations are biodegraded as readily.
- (e) There are conflicting data about the completeness of TNT degradation. One report indicates that TNT can be mineralized via composting (Osmon and Andrews, 1978), but all other researchers have found transformation products of unknown toxicity or mutagenicity.

3.4.5.3 Comments.

- (a) The feasibility and expense of this technology depend on the existing facilities and the selected method.
- (b) TNT will not transform if it has sorbed onto the soil.
- (c) It is possible that 2,4-DNT would mineralize naturally with time, and induced degradation would not be necessary (Isbister et al., 1980).
- (d) Of the TNT that undergoes transformation, 99 percent produces two initial conversion products, i.e., 2-amino and 4-aminodinitrotoluene, and their condensation products (Isbister et al., 1980).
- (e) Heavy metals will be bioaccumulated by aerobes and may reach concentrations toxic to the microbes.



3.4.5.4 References.

- (a) Weston, Roy F., Inc., "The Cost Estimating Guide for Municipal Wastewater Treatment," Currently in draft form.
- (b) Coia et al., 1983.
- (c) Sundstrom and Klei, 1975.
- (d) Benefield and Randall, 1980.
- (e) Isbister et al, 1980.
- (f) Spanggord et al., 1980.
- (g) Burlinson, 1980.
- (h) Osmon and Andrews, 1978.
- (i) Chambers et al., 1963.
- (j) McCormick et al., 1981.
- (k) Carpenter et al., 1978.
- (1) Wendt et al., 1978.
- (m) McCormick et al., 1978.
- (n) Kaplan and Kaplan, 1982.
- (o) Hale et al., 1979.
- (p) Conway and Ross, 1980.
- (q) Personal communication with Dr. Spanggord, SRI, 3 August 1983.



- 3.4.6 Aerobic biodegradation -- activated sludge.
- 3.4.6.1 Description. This is a method of biological oxidation caused by a native bacterial culture in an aerated tank. The organic contaminants are metabolized to ${\rm CO}_2$, ${\rm H}_2{\rm O}$, and biomass. Figure 37 illustrates this process.

The contaminants are put into solution, and inert solids are separated out. The solution is then put into a well-mixed activated sludge tank. The residence time is determined by the rate of degradation.

Microbial populations are recycled to maintain their numbers and the desired food:microorganism ratio. The excess sludge is usually further anaerobically digested to ensure stabilization.

- 3.4.6.2 Applicability. Refer to subsection 3.4.5, "Aerobic biodegradation."
 - (a) This process is used commercially for wastewater treatment, especially sewage.
 - 3.4.6.3 Comments.
 - (a) The feasibility of this process depends on the availability of existing facilities; it is expensive if facilities must be built.
 - (b) This process is more suitable to soils contaminated with significant concentrations of organic pollutants that can support biological growth.

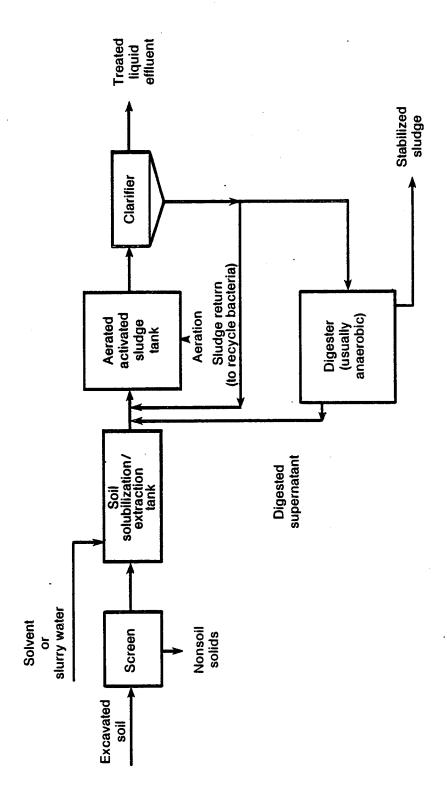


Figure 37. Aerobic biodegradation — activated sludge treatment.



- 3.4.7 Aerobic biodegradation--rotating biological contactor (RBC).
- 3.4.7.1 Description. A rotating biological contactor (RBC) is an aerobic contactor consisting of polystyrene discs mounted on a central shaft. The RBC is half submerged in a tank containing organics-contaminated wastewater (or, in this case, a slurry or extract of the contaminated soil). The discs are rotated at 1 to 30 rpm so the surface is exposed to ambient air and liquid alternately. The process diagram is shown on Figure 38.

Bacterial growth forms on the discs and metabolizes the organics present in solution. Oxygen uptake occurs as the surface rotates through the air. Excess biomass is sloughed off as the discs pass through the liquid, and kept in solution through the motion of the RBC.

- 3.4.7.2 Applicability. Refer to subsection 3.4.5, "Aerobic biodegradation."
 - (a) RBC's are widely used for wastewater treatment. Pilotand full-scale units are readily available.

3.4.7.3 Comments.

- (a) RBC's have lower operating costs and are easier to maintain than activated sludge units, but their capital costs are higher.
- (b) RBC's can be staged with or without an intermediate clarifier. A final clarifier is necessary, however.

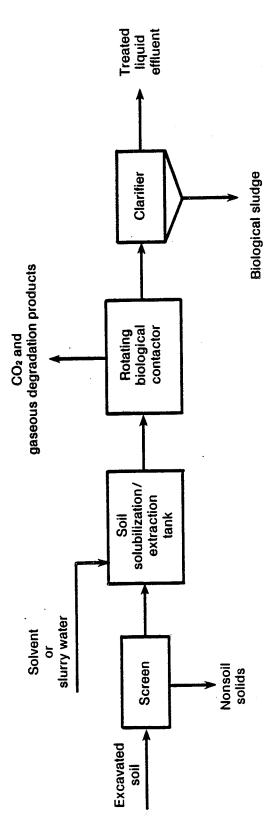


Figure 38. Rotating biological contactor.



- 3.4.8 Aerobic biodegradation -- bioponds.
- 3.4.8.1 Description. Bioponds may be constructed, or existing nearby lagoons may be used. The organics-contaminated soil is added to the water-filled pond. Frequent dredging may be necessary to loosen settled soil. An aerator/mixer provides aeration for the microbes and keeps the contaminants in solution. Microbes may be naturally-occurring, or may have to be introduced into the biopond.
- 3.4.8.2 Applicability. Refer to subsection 3.4.5, "Aerobic biodegradation."
 - 3.4.8.3 Comments.
 - (a) This process is relatively inexpensive, especially if land is available for ponds.
 - (b) Cold weather affects treatment efficiency.
 - (c) Water-soluble organics are more readily degraded than insoluble compounds.
 - (d) This process is more suitable for the treatment of soil extracts.
 - (e) A pond liner may be required.



- 3.4.9 Fluidized bed biological treatment.
- 3.4.9.1 Description. An inert medium (often sand or plastic packings) is suspended by the upflow of organics-contaminated wastewater through a column. This fluidization increases the surface area available for biological growth. Aerobic conditions are maintained by gaseous O₂ dissolved into the wastewater feed stream. Aerobic biodegradation of the organics leaves a sludge residue.
 - 3.4.9.2. Applicability.
 - (a) This process is applicable to the biodegradability of explosives (see subsection 3.4.5, "Aerobic biodegradation").
 - (b) There are at least eight commercial units for wastewater treatment.
 - 3.4.9.3 Comments.
 - (a) This process is suitable for the treatment of liquid and slurry wastes.
 - (b) Metals will accumulate in the waste sludge. Certain other inorganic compounds will be converted; e.g., NH3 will transform to NO3.
 - 3.4.9.4 References.
 - (a) Sundstrom and Klei, 1975.



3.4.10 Landfarming.

3.4.10.1 Description. Microbial populations in the soil are concentrated in the plow-zone, the top 6 to 8 inches of soil. Landfarming incorporates the contaminated soil into this upper soil zone to allow microbial biodegradation of organics. Other important reactions occur; i.e., reduction/oxidation of organics, volatilization, and leaching.

The downward movement of explosives through soil is known to be a slow process. If the explosives are near the surface, land-farming would be done in-situ with the addition of some nutrified soil and plowing, assuming the soils are nonexplosive when agitated.

3.4.10.2 Applicability.

- (a) Landfarming is often used for agricultural land. The petroleum industry first adapted it for commercial purposes to dispose of biodegradable oily solids. The chemical and pharmaceutical industries also use landfarming for waste disposal.
- (b) Explosives can only be landfarmed if they can first be stabilized or diluted to prevent detonation.
- (c) Landfarming is not effective for wastes with high metals concentrations.

3.4.10.3 Comments.

- (a) The low cost and simplicity of landfarming are its primary advantages.
- (b) Conditions such as temperature, moisture, and aeration are difficult to control. The suboptimal conditions make landfarming a slower process than composting or aerobic biodegradation.
- (c) Landfarming could be used as a treatment process for organic sludges resulting from other treatment schemes.

3.4.10.4 References.

- (a) Pojasek, 1978.
- (b) Huddleston, 1979.
- (c) "Treatment and Disposal of Industrial Wastewaters and Residues," 1978.
- (d) Ndu et al., 1978.
- (e) Devitt et al., 1976.
- (f) Wilson et al., 1981.



- (g) (h)
- Crosby et al., 1968.
 Smith et al., 1977.
 Technology transfer conference with Dr. Kirk Brown, 1 July 1983. (i)



- 3.4.11 Anaerobic biodegradation.
- 3.4.11.1 Description. In this process waste-acclimated microorganisms are mixed in with contaminated waste and kept in an oxygen-free atmosphere to maintain anaerobic conditions in order to decompose organics. A process diagram is shown on Figure 39.

An anaerobic digester is the usual reactor, and the system temperature is kept at about 35° C. Frequent mixing is needed to ensure adequate contacting. The usual residence time is 12 to 30 days.

3.4.11.2 Applicability.

- (a) Anaerobic digestion is commercially used for wastewater treatment. Explosives degradation has only been tested on a laboratory scale.
- (b) Anaerobic conditions are difficult to establish with large volumes of soil. Excavation and the use of digesters are expensive.
- (c) Low concentrations of RDX can be anaerobically degraded ed rapidly and completely. Anaerobic degradation products include methanol, methane, hydrazine compounds, CO2, and formaldehyde, which further degrades. (There is a conflict in data concerning the toxicity and mutagenicity of the products and intermediates.)
- (d) Anaerobes have not been found that can degrade TNT, DNT, glycerol nitrates, and RDX above 50 mg/L. TNT and DNT will partially transform with anaerobic microbes.
- (e) Halogenated aromatics will degrade anaerobically.
- (f) The presence of heavy metals slows the degradation of organics. It is possible to precipitate metal sulfides to remove the metals from the digester.

3.4.11.3 Comments.

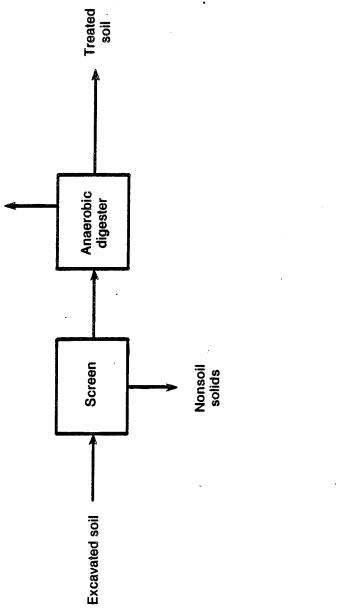
(a) The gaseous methane that is produced can be burned to supply energy. Other products are gaseous ${\rm H}_2{\rm O}$ and ${\rm CO}_2$.

3.4.11.4 References.

(a) Weston, Roy F., Inc., "The Cost Estimating Guide for Municipal Wastewater Treatment," currently in draft form.



- Sundstrom and Klei, 1975. (b)
- Benefield et al., 1980. Isbister et al., 1980. (c)
- (d)
- Spanggord et al., 1980. McCormick et al., 1981. (e)
- (f)



CH4, CO2, degradation products

Figure 39. Anaerobic digestion.



- 3.4.12 Anaerobic/aerobic cycling.
- 3.4.12.1 Description. A system utilizing cycling will degrade organic contaminants that are susceptible to either aerobic or anaerobic digestion. The system has the flexibility to treat a wider variety of contaminants since it provides both anaerobic and aerobic conditions. For example, a system utilizing cycling will degrade RDX in the anaerobic cycle and will degrade 2,4-DNT in the aerobic cycle.

An existing lagoon can be used as a biopond, or a biopond can be constructed, and anaerobic microbes mixed in by dredging. After RDX is degraded, the biopond is drained to allow aerobic composting, or an aerator/mixer is used with a flooded pond. Aerobic microbes are introduced to complete the degradation.

Other methods of effecting anaerobic/aerobic cycling can be used. For instance, a series of RBC's can be adapted for this application. Conventional treatment equipment may also be used; e.g., the anaerobic digester is often implemented with the aerobic activated sludge treatment.

- 3.4.12.2 Applicability. Refer to subsection 3.4.5, "Aerobic biodegradation," and 3.4.11, "Anaerobic biodegradation."
 - (a) Cycling will degrade RDX and DNT. However, the effect on TNT is unknown. There are possible toxic by-products associated with this technology.
 - (b) Heavy metals may hinder both the aerobic and anaerobic steps of the cycling process.
 - 3.4.12.3 Comments.
 - (a) Studies are needed to determine the relative cycling times.
 - (b) Anaerobically digested sludge is toxic to some aerobic organisms. In these cases, the aerobic step should precede the anaerobic treatment.
 - 3.4.12.4 References.
 - (a) Isbister et al., 1980.
 - (b) Technology transfer conference with Dr. Kirk Brown at West Chester, Pennsylvania on 7 July 1983.



- 3.4.13 Biodegradation -- use of adapted microbial cultures.
- 3.4.13.1 Description. This process involves the development of adapted or artificially-engineered microorganisms to effect the biodegradation of recalcitrant organic compounds. This is a relatively new technology, publicized by a 1980 Supreme Court ruling on the patentability of an oil-eating bacterium developed by Dr. Ananda Chackrabarty.

Dr. Ronald Spanggord reported the discovery of naturally-acclimated microbes that completely mineralize 2,4-DNT and partially degrade other DNT isomers, including the recalcitrant 2,6-DNT. The microbes were found in a bay downstream from an Army facility, and degradation rates were slow until the researchers increased the microbial population.

Dr. Spanggord feels that this finding could eventually be transferrable to TNT or 2,6-DNT degradation. Research would be directed toward genetic engineering with plasmid material.

3.4.13.2 Applicability.

- (a) Engineered microbes would be needed to permit the following:
 - 2,6-DNT degradation; currently only SRI reports even partial degradation.
 - Complete TNT degradation without conversion to toxic transformation products.
 - RDX aerobic degradation.
 - RDX degradation (anaerobic) at higher concentrations of RDX.
- (b) Engineered microbes may also be effective in decomposing the solvents and grease found in contaminated soil.
- (c) Heavy metals are bioaccumulated by microbes and may reach toxic concentrations.

3.4.13.3 Comments.

- (a) Bioengineering firms that were contacted report no current research in the cultivation of adapted cultures for explosives biodegradation (Genex, Genentech, Polybac). Genex would be interested in research.
- (b) This area of research is very time consuming. Researchers predict 5 to 10 years would be needed to develop this technology if a research program was undertaken.



The low explosives concentrations in the soil have pre-(c) vented the acclimation of natural microbes that could degrade explosives.

When the levels of contaminants have fallen, naturally-(d) occurring microbes consume the foreign bacteria.

3.4.13.4 References.

- "New Technology," Chemical Engineering, 1983. Isbister et al., 1980. (a)
- (b)
- Spanggord et al., 1980. (C)
- "Rutgers Student Develops System to Treat Waste with (d) Microbes, " Hazardous Waste News, 1983.
- Jones et al., 1981. (e)
- Personal communication with Jean Brenchley, Genex Cor-(f) poration, 4 August 1983.
- with Genentech Corporation, Personal communication (g) 4 August 1983.
- Personal communication with Dr. Ronald Spanggord, SRI, (h) 3 August 1983.



3.4.14 Vegetative uptake.

3.4.14.1 Description. Certain plants growing on contaminated soil will selectively uptake heavy metals and concentrate them within their tissues. The amount of this uptake is determined by the availability of the element to the plant, as measured by the solubility of the metal in water. The metal-laden plants are subsequently incinerated.

3.4.14.2 Applicability.

- (a) Uptake has been demonstrated for many heavy metals; e.g., arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. Some metals are not accumulated in significant amounts, such as plutonium, radium, thallium, and uranium (Army, 1980).
- (b) Organics that are recalcitrant to degradation can be accumulated by plants. The uptake of organics, however, is usually small compared to the uptake of metals. Very little uptake occurs with RDX (Atlantic Research, 1979), and no data are available for other organic explosives.
- (c) With time, certain metals in soils may convert to forms unavailable to plants. This pnenomenon, called reversion, is not well understood. It is not known if this transformation is reversible.
- (d) "Aquaculture" is a developmental technology using vegetative uptake by aquatic plants. Experimental systems use the water hyacinth to remove nutrients, BOD5, metals, and suspended solids from wastewater. Metals accumulation has also been widely studied with seaweed, duckweed, and alligator weed.

3.4.14.3 Comments.

- (a) If the metals content in a plant becomes too high, further plant growth will be suppressed. This phytotoxic effect is most frequently noted with arsenic and cadmium. Certain soil additives, known as Lewatit cation exchangers, can counteract this effect, but these will inhibit the uptake of metals.
- (b) Vegetative uptake is highly dependent on soil acidity; metals removal will not be significant in neutral or basic soils.
- (c) Other parameters that affect uptake include plant species, soil chemistry, moisture, and type of metal.



3.4.14.4 References.

- (a) "Treatment and Disposal of Industrial Wastewaters and Residues," 1978.
- (b) Harward et al., 1980.
- (c) Weston, Roy F., Inc., "The Cost Estimating Guide for Municipal Wastewater Treatment," currently in draft form.
- (d) Van Assche and DeMay, 1977.
- (e) Wentsel et al., 1979.
- (f) Cherry and Guthrie, 1979.
- (g) Lee et al., 1982.
- (h) Lyngby et al., 1982.
- (i) Mahler et al., 1980.
- (j) Rodgers et al., 1978.
- (k) Ndu et al., 1978.



- 3.4.15 Bioreclamation of soils: groundwater decontamination system (GDS).
- 3.4.15.1 Description. This process is designed to eliminate hydrocarbons and halogenated hydrocarbon contaminants from groundwater and soil through a process of accelerated biodegradation by microorganisms existing in the contaminated soil. Contaminated groundwater is pumped into the activation tanks (see Figures 40 and 41) where the biodegradation rate is increased exponentially by providing air and nutrients. The water is continuously recirculated in the activation tank to ensure the dispersal of the organisms throughout the tank. This also prevents the air diffusers from becoming clogged with settling sludge. The temperature is maintained between 18 and 22°C. The effluent from the activation tank is pumped into the settling tank at the same rate as the feed groundwater.

The settling tank residence time is regulated by the activating tank with a temperature range of 8 to 22°C. The organisms (biomass) settle to the bottom of the tank and are returned to the activation tank. The decanted water, rich in organisms, nutrients and oxygen, is pumped into the reinjection trenches at a rate that maintains the residence time in the treatment system.

This water acts as an initiator of in-situ biodegradation and as a solvent, dissolving water-soluble contaminants. The groundwater collects in the dewatering wells where it is pumped to the activation tanks to complete the process cycle.

3.4.15.2 Applicability.

- (a) The GDS system is available commercially.
- (b) The system has been employed to decontaminate soils and groundwater of methylene chloride, n-butyl alcohol, acetone, and dimethylaniline on a commercial scale.
- (c) No experience with explosives is reported at this time.
- (d) Heavy metals may hinder biodegradation in soils.

3.4.15.3 Comments.

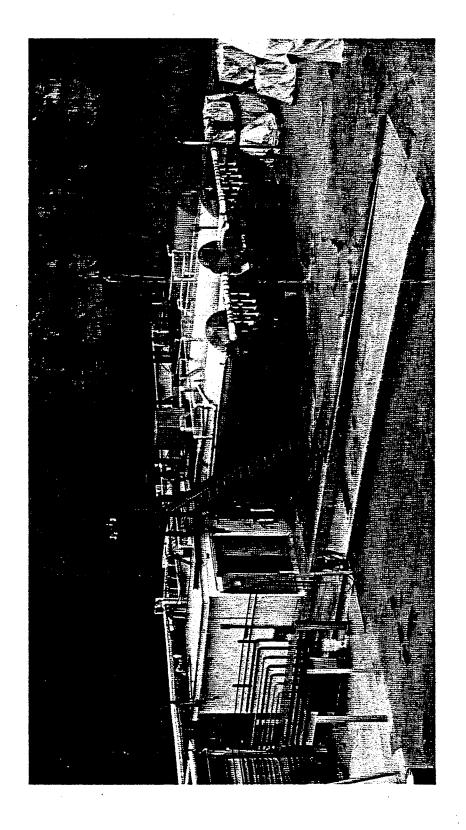
- (a) Biological sludge is separated in the settling tank and will require further treatment and disposal.
- (b) The existing operation treats 12,000 gallons/day of groundwater at a cost of \$0.02/gallon.



3.4.15.4 References.

- (a) Jhaveri and Mazzacca, 1982.
- (b) Personal communication with Alfred Mazzacca, Groundwater Decontamination Systems, Inc., 15 July 1983.

Figure 40. Process schematic GDS system.





3.5 Physical processes.

3.5.1 Secure landfills.

5.5.1.1 Description. These are landfills specifically designed and constructed to isolate contaminated wastes from air, surface water, and groundwater, as shown on Figure 42. They differ from conventional landfills that incorporate the fill into the ecosystem to some degree.

Contaminated waste, sometimes pretreated, is dumped into the landfill basin. The basin is lined with an impermeable material that prevents leachate from reaching the groundwater. The liner may be a synthetic polymeric membrane, the compacted natural clay of the site, or a double lining of the two materials.

A leachate control system is installed to monitor and remove leachate and any rainwater that falls during filling operations.

As filling continues, incompatible contaminants must be segregated. A spatial record of the fill is kept so that if recovery techniques are developed, the location of a particular contaminant is known.

Each day a layer of uncontaminated soil is spread over the fill. The completed landfill is capped with a layer of compacted clay and/or a synthetic liner. The fill is then covered with a layer of topsoil.

3.5.1.2 Applicability.

(a) Secure landfills are widely used for toxic wastes.

(b) Triangle Resource Industries, a division of SCA Chemical Services, will handle explosives in their landfills, if they have been desensitized. Metals-laden wastes are frequently landfilled.

(c) Siting can be difficult due to hydrogeological constraints; the cost of transport is also an important consideration.

3.5.1.3 Comments.

(a) Secure landfills are considered to be a cost-effective alternative when transport costs are not significant. However, SCA says that the cost is higher when explosives are involved.

Figure 42. Typical secure landfill.



- (b) Groundwater must be monitored to detect any liner failure. Certain investigators believe that some degree of leakage is inevitable and will undermine the effectiveness of a "secure" landfill (Piasecki, 1983).
- (c) Secure landfills should not be used if the waste will generate any harmful vapors.

3.5.1.4 References.

- (a) Shultz, 1981.
- (b) Pojasek, 1980.
- (c) "Treatment and Disposal of Industrial Wastewaters,"
 1977.
- (d) Lancaster and Bulkely, 1983.
- (e) Piasecki, 1983.
- (f) EPA, "Guide to the Disposal of Chemically Stabilized and Solidified Waste," 1980.
- and Solidified Waste, 1980.

 (g) Personal communication with Jim Knowles, Triangle Resource Industries, a division of SCA Services, 12 and 28 September 1983.



3.5.2 Slurry wall.

3.5.2.1 Description. Slurry walls provide impenetrable subsurface barriers to any lateral migration of the contaminants present at a specific site. A trench is constructed that is 3 to 5 feet wide and deep enough to connect with the impervious aquiclude. Trench construction is either by excavation or by vibrated beam injection of a self-hardening slurry. During excavation, the trench is filled with a slurry of bentonite clay and water.

The hydrostatic pressure of the slurry on the trench walls prevents their collapse. Excavation in the water-saturated soil below the surface of the water table forms trench walls that are particularly susceptible to collapse. The slurry also produces a low-permeability filter cake of bentonite that lines the trench walls and bottom. The trench is then backfilled with a material of low permeability. Common fills are soil-bentonite, cement-bentonite, and concrete. Cement-bentonite, or coulis, is a self-hardening slurry and backfilling is not necessary.

3.5.2.2 Applicability.

- (a) The expense and feasibility are site-specific, depending on location, ease of access, geography, etc.
- (b) Explosives are thought to migrate through the soil very slowly, and may not endanger the groundwater. Slurry walls are more useful in containing solvents, which generally migrate rapidly through soils.
- (c) Slurry walls have been used in the construction industry since the 1940's. Europeans have also used the walls to contain lagoons and control the water table, but slurry walls are a relatively new technology in the United States. A typical application of slurry wall containment is shown on Figure 43.

3.5.2.3 Comments.

- (a) Slurry walls only contain the contaminants, and so are usually used in conjunction with desensitization methods.
- (b) The presence of certain organic chemicals can alter the permeability of the wall.
- (c) The leachate area must be carefully defined to avoid excavation into explosives-laden soil.
- (d) Vendor information is readily available. Costs vary by location, accessibility, and the type of backfill. Cement backfill, for instance, is four times as costly as earthen material.



3.5.2.4 References.

- Coia et al., 1983. (a)
- (b)
- Spooner et al., undated. Vendor information from Slurry Systems, a division of Thatcher Engineering Corporation, Gary, Indiana. (c)

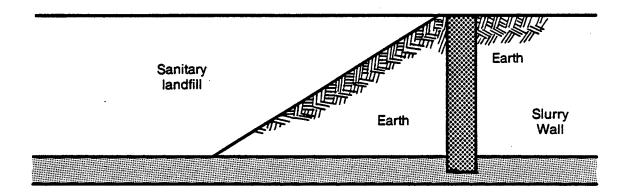


Figure 43. Typical application of a slurry wall.



3.5.3 Grouting.

3.5.3.1 Description. Grout injection installs an impenetrable subsurface barrier that prevents the migration of contaminants. An injection hole is constructed either with a vibrated beam or a drill. A thixotrophic fluid material is pressure injected into the soil or rock. Grouting materials can be either certain Newtonian chemicals (e.g., bitumens, organic polymers) or colloidal suspensions of cement or bentonite in water. The fluid sets, producing a strong solid with low permeability. The hardened grout has a low permeability and will be an effective barrier to groundwater migration.

There are three types of grout:

Area blanket grout -- for sealing shallow soils. (a)

High pressure or "jet" grout -- for use at depth, to (b) seal a slurry wall panel (concrete walls are in-

stalled as panels) to the aquiclude.

Contact -- to seal water flow passages at the outer (C) surface of an excavation. It can be used when a slurry wall cannot be directly connected to the aquiclude because of a rock formation that would be difficult to excavate. Figure 44 illustrates a typical application of grout injection.

3.5.3.2 Applicability.

Grouting is most commonly used for tunnel and dam construction, with the grout strengthening the soil or rock and not permitting water to pass.

EPA is studying this process as a method of isolating (b) disposal sites with a grout lining on the bottom and

the walls.

Grouting has not been used extensively, and is still in (C) the development stage as a method for groundwater control.

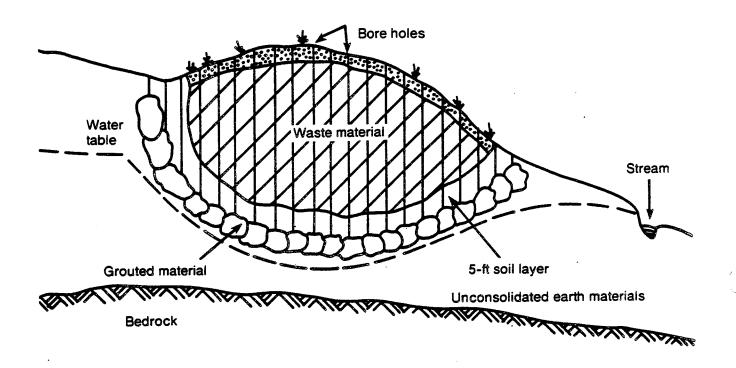
Because grouting is only a containment technology, it (d) would most likely be used in conjunction with a de-

sensitization technology.

explosives is slow, The downward migration of (e) groundwater may not be endangered. Solvents migrate more rapidly, however.



- 3.5.3.3 Comments.
- (a) Grout injection is more expensive than slurry wall construction.
- (b) Compatibility considerations are important since certain chemicals increase the permeability of the grout material.
- 3.5.3.4 References.
- (a) Coia et al., 1983.



Source: Tolman et al, 1978

Figure 44. Cross-section of grouted bottom seal beneath a containment area.



3.5.4 Geological isolation.

3.5.4.1 Description. Contaminated waste is removed from its site and placed in a geological structure. The waste remains accessible if it is stored in a salt dome in stratified rock.

A more permanent option is sea bed disposal. Hazardous waste containers are implanted in the ocean sediment "tens of meters" deep. Sites are chosen for the presence of "red-clay" sediment that is unconsolidated and fine grained. The clay has low permeability and its sorptive properties will impede movement of escaped particles. The sediment is not very strong, reducing the difficulty of excavating a subsurface storage area.

A variation of seabed disposal would be the use of very deep drill holes (25,000 feet deep). This is an established technology from deep-sea drilling, and methods could be adapted from the technology used to construct mined repositories for waste storage.

3.5.4.2 Applicability.

- (a) Low-level radioactive wastes (i.e., any waste that will be hazardous for 10 to 100 years) are currently disposed of in sea beds by many European countries such as Switzerland, Belgium, and the United Kingdom.
- (b) Sea bed disposal is expected to be approved by the EPA in the mid-1980's. Radioactive wastes in the United States are frequently stored in salt mines, but other options are being explored.
- (c) The Department of Energy (DOE) is investigating the possibilities of geological isolation of high-level radioactive wastes.

3.5.4.3 Comments.

- (a) The siting of disposal sites is important, since the structure must be in a geologically-stable environment. Sea bed stability is particularly difficult to determine.
- (b) Waste is often pretreated or placed in a container to further isolate contaminants.
- (c) This process is considered an expensive treatment and is not suitable for large volumes of waste.

3.5.4.4 References.

- (a) Pojasek, 1980.
- (b) Lancaster and Bulkely, 1983.



- 3.5.5 Fixation (pretreatment).
- 3.5.5.1 Description. Fixation processes improve the physical or chemical condition of a waste to minimize its movement within a contaminated site. Fixation can be a precursor to another treatment or it can be the final step before disposal. The two types of treatment are chemical treatment (e.g., pH adjustment) and solidification (e.g., stabilization, encapsulation). These will be discussed in detail in subsequent subsections.

Many wastes require chemical pretreatment to remove contaminants that are incompatible with each other or with the subsequent treatment process. Solidification is performed to transform the waste into a more convenient form for transport or disposal and to prevent leaching. The goal of fixation is to permit final disposal in a nonsecured landfill.

TABLE 7. APPLICABILTY OF FIXATION FOR SPECIFIC CONTAMINANTS

Process	Heavy metals	Organic solvents ^a	Solid organics (excluding explosives)	Acidic wastes (from explosives manufacturing)	Oxidants	Sulfates
Microencapsulation		,				
Asphalt-based	Applicable	Applicable	Applicable; contaminant may act as a binding agent	Applicable if waste is first neutralized	Not applicable	Not applicable
Polymer-based	Applicable	Applicable, impeded set- ingb	Applicable, impeded setting	Applicable	Not applicable	Applicable
Macroencapsulation with polyethylene	Applicable	Applicable if contami- nant is ad- sorbed onto a solid	Applicable	Applicable if waste is first neutralized	Not applicable	Applicable
Stabilization						
Cement-based	Applicable	Applicable; impeded set- ting	Applicable	Applicable (contaminant is neutralized by the basic cement)	Applicable	Applicable if an additive is used to prevent spalling
Pozzolanic	Applicable	Applicable; impeded set- ting	Applicable	Applicable	Applicable	Applicable

^aMay volatilize upon heating. ^b"Impeded setting" does not preclude the existence of an additive that could counteract this effect.



3.5.6 Microencapsulation.

3.5.6.1 Description. In this process, excavated waste is mixed with an inert immobilizing agent in an on-site extruder operating at 130 to 230°C. When the mixture solidifies, contaminant particulates are dispersed and encased within a matrix. Matrix materials are thermoplastics such as asphalt, paraffin, bitumen, and certain organic polymers such as polyethylene or polystyrene. The matrix:waste ratio varies from 1:1 to 1:2 on a dry weight basis.

The solid product has a low permeability to prevent leaching. The contaminant is isolated from the environment in a solid that is resistant to weathering or biological attack. A secondary container, such as a polyethylene jacket or a steel drum, may be used to prevent surface leaching. The contained waste is then disposed of in a nonsecure landfill, or could possibly be used as a construction material.

A variation of this process is returning the extruded material to the excavated site and letting it harden in the ground.

3.5.6.2 Applicability.

- (a) Microencapsulation is most commonly used for high toxicity, low volume wastes.
- (b) The cost of this process depends on the choice of matrix material; however, it is considered a more expensive treatment than secure landfills. Organic polymer agents are substantially more expensive than other matrix materials.
- (c) The EPA says explosives are not suitable for microencapsulation, but a number of vendors, such as Lopat Enterprises, Inc., are willing to experiment with explosives-laden wastes.
- (d) The extrusion of explosives has an unknown feasibility -- it is unknown if the high temperatures needed for thermoplastics will be safe for explosives. Pretreatment to remove or stabilize volatile compounds might be necessary.
- (e) Mobile equipment is used for microencapsulation; operating costs are high.

3.5.6.3 Comments.

(a) Certain organic compounds will dissolve organic thermoplastic materials; asphalt can then be used as the immobilizing agent in these cases.



- (b) If the solid matrix is fractured, leaching of waste will occur. Final disposal must avoid endangering the physical integrity of the solid.
- (c) Many of the vendors of microencapsulation processes own the exclusive patent rights to their specific matrix material.
- (d) S-Cubed Company is currently investigating sludge encapsulation techniques for USATHAMA. Their report is expected in the fall of 1983.

3.5.6.4 References.

- (a) Shultz, 1980.
- (b) Beaudet et al., 1983.
- (c) Pojasek, 1980.
- (d) Pojasek, 1978.
- (e) Weston, Roy F., Inc., Confidential communication, 1982.
- (f) Coia et al., 1983.
- (g) Lancaster and Bulkely, 1983.
- (h) EPA, "Guide to the Disposal of Chemically Stabilized and Solidified Waste," 1980.
- (i) Personal communication with Louis Flax, Lopat Enterprises, Inc., 12 September 1983.
- (j) Vendor information from Lopat Enterprises, Inc., Asbury Park, New Jersey.
- (k) Personal communication with Dr. Eli Misheck, S-Cubed Company, 7 September 1983.



- 3.5.7 Stabilization (chemical admixing).
- 3.5.7.1 Description. Similar to microencapsulation, stabilization also immobilizes the waste within a solid matrix. Stabilization, however, involves a chemical reaction that binds the waste to the admixture material. This chemical affinity stabilizes the resulting solid to make it more resistant to chemical and mechanical stresses.

waste is slurried with water and mixed with a fixation agent. The mixture that is produced dries as water either evaporates or is consumed in the binding reaction. The resulting solid has low permeability and can be discharged directly into an unsecured landfill and allowed to set. Because of the stability of the rock-like product, a secondary container is seldom used, although a surface sealant may be necessary to prevent leaching.

There are two types of fixation processes, i.e., cement-based and pozzolanic. Cement-based fixation (see Figure 45) uses powdered portland cement as the stabilization agent. Cementation occurs with the addition of water to the anhydrous powder. Pozzolanic fixation (see Figure 46), also called lime-based fixation, uses a blend of lime and a siliceous material such as fly ash. This mixture will react with water to form pozzolanic concrete.

The final solid has physical strength, but the monolith is not resistant to weathering. A disposal alternative is using the solid as a construction material. Stabilization products have been used for runway and roadway foundations and dike supports.

3.5.7.2 Applicability.

- (a) Stabilization is an established technology in Europe and the United States, especially for radioactive wastes and heavy metals.
- (b) Inorganic wastes are easily stabilized. Metals will form insoluble metal hydroxides and carbonates.
- (c) Organic concentrations above 10 percent can have a detrimental effect on matrix stability. Also, certain contaminants may act as setting retarders. Additives are available that can counteract these problems, however.
- (d) Stabilization is best suited for high volume, low toxicity wastes.



(e) The EPA says that explosives should not be stabilized, but a number of vendors are willing to experiment with explosives stabilization, such as Conversion Systems, Inc., Horsham, Pennsylvania.

(f) S-Cubed Company, California is currently investigating stabilization of sludges under a USATHAMA contract. Their report is expected in the fall of 1983.

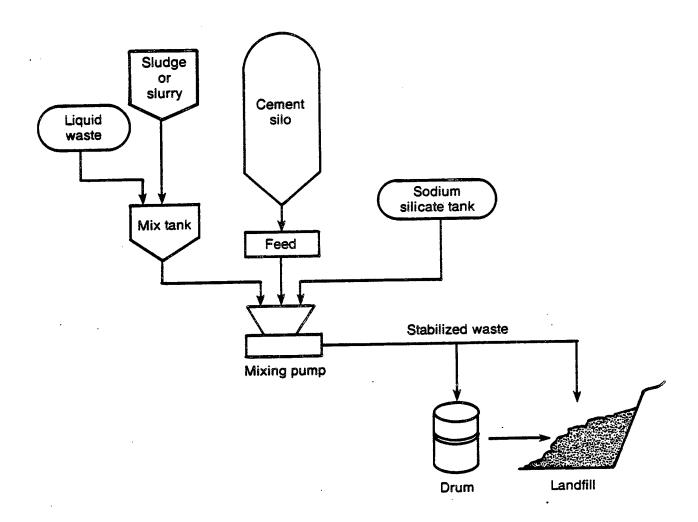


Figure 45. Cement-based stabilization process.

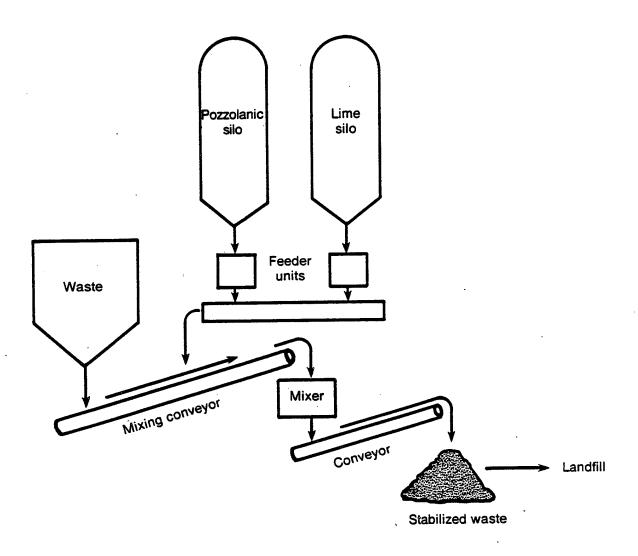


Figure 46. Lime-based (pozzolanic) stabilization process.



3.5.7.3 Comments.

- (a) Many pozzolanic agents are materials that are waste products themselves, such as fly ash, cement-kiln dust, and ground blast-furnace slag.
- (b) Mobile on-site treatment units make this an inexpensive option.
- (c) Stabilization products are considered more stable than encapsulated wastes. Also, if the matrix is fractured, stabilized wastes are safer since there will be no pure contaminant particulates to leach into the soil.

3.5.7.4 References.

- (a) Shultz, 1981.
- (b) Beaudet et al., 1983.
- (c) Pojasek, 1980.
- (d) Pojasek, 1978.
- (e) Weston, Roy F., Inc., Confidential communication, 1982.
- (f) Coia et al, 1983.
- (g) EPA, "Guide to the Disposal of Chemically Stabilized and Solidified Waste," 1980.
- (h) Personal communication with Dr. Eli Misheck, S-Cubed Company, 7 September 1983.



3.5.8 Macroencapsulation ("jacketing").

3.5.8.1 Description. In this process dried waste is pressed together under high temperature and pressure to induce fusion. An inert polymer coating, such as polyethylene or a urea-formal-dehyde (UF) system, is fused around the solid block and dried. The contaminant is thus isolated from environmental forces and may be disposed of in a nonsecure landfill.

One variation has resulted from the problems encountered due to lack of adhesion between the coating and the fused waste block. A binding agent may be mixed in with the waste, and adhesion is improved through the chemical affinity between the jacket and the binding agent.

3.5.8.2 Applicability.

(a) This is a well-developed technology used for both organic and inorganic wastes. There was no vendor information specifically for explosives jacketing.

(b) Mobile on-site treatment units are used, but this is still an expensive process because of the costs of drying; also, resin is more expensive than stabilizing agents.

(c) Dried soils contaminated with explosives are known safety hazards.

3.5.8.3 Comments.

(a) Polyethylene is combustible, and the method of final disposal must consider this hazard.

(b) It is advantageous to reduce the volume of contaminated material by pretreating the waste with volume reduction techniques (e.g., stripping, extraction, etc.).

(c) If the jacket is fractured, contaminants will be released. Final disposal should be designed to avoid undue mechanical stresses that could breach the coating material.

(d) Less reagent is needed with macroencapsulation than with microencapsulation or stabilization. However, organic polymer reagents are substantially more expensive than other fixation agents.

3.5.8.4 References.

- (a) Shultz, 1981.
- (b) Pojasek, 1980.



- (c) Pojasek, 1978.
- (d) "Treatment and Disposal of Industrial Wastewaters and Residues," 1977.
- (e) Weston, Roy F., Inc., Confidential communication.
- (f) Coia et al., 1983.
- (g) EPA, "Guide to the Disposal of Chemically Stabilized and Solidified Waste," 1980.
- (h) Lubowitz and Tells, 1981.

- 3.5.9 High gradient magnetic separation (HGMS).
- 3.5.9.1 Description. HGMS removes weakly magnetic and non-magnetic submicron-sized particles by capturing them on a magnetized surface. A matrix of filamentous ferromagnetic material provides the surface area for the collection of the paramagnetic molecules. Common matrix materials are stainless steel wool and expanded metal packing.

Contaminated waste is either slurried or transported by air. A solenoid is used to generate a uniform field of 1,000 to 20,000 gauss. (A magnetic separator is illustrated on Figure 47.) The retained particles are recovered when the field is turned off and the matrix is flushed with liquid.

Certain nonmagnetic materials may be removed by "seeding" with a ferromagnetic substance, such as colloidal Fe $_2$ O $_3$. This creates an agglomerate with paramagnetic properties.

3.5.9.2 Applicability.

- (a) HGMS was first commercialized in 1974 for continuous removal of mineral impurities from clay slurries. Other current applications include: beneficiation of low-grade ores, recovery of metals (e.g., nickel, iron, chromium) from processing wastes, and removal of iron from river water.
- (b) HGMS is also capable of treating solid wastes. One of the most common applications is coal desulfurization and demineralization. Continuous separators can process a flow of 100 tons of dry coal per hour, removing 93 percent of the pyritic (inorganic) sulfur. HGMS has proven as effective as the conventional flotation process for minerals removal.
- (c) Although pilot studies are underway for mobile treatment units, all current applications use permanent installations.
- (d) Capital outlay varies with the strength of the required magnetic field. Operating costs are estimated at \$1 to \$5/1,000 gallons for removal of paramagnetic particles from liquids (Metry, 1982).

3.5.9.3 Comments.

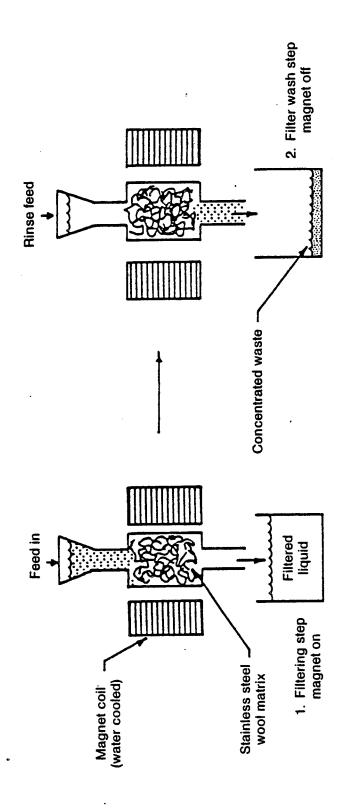
(a) The most important variable affecting efficiency is the strength of the magnetic field. Other significant parameters include: residence time, matrix packing density, temperature, and pH.



- (b) HGMS can handle flow rates more than 100 times faster than those found with conventional filtration.
- (c) This process has become a more economical option in the past few years. For many applications, it is now considered to have lower operating costs than other conventional metals removal processes, such as flotation (Hucko and Miller, 1980).
- (d) HGMS has been found to operate more efficiently with a water slurry feed than with air dispersion of contaminated wastes.

3.5.9.4 References.

- (a) Shultz, 1981.
- (b) Kiang and Metry, 1982.
- (c) Kolm et al., 1975.
- (d) Appleton and Dobbing, 1976.
- (e) de Latour, 1976.
- (f) Liu, 1982.
- (g) Watson, 1979.
- (h) Hucko and Miller, 1980.
- (i) Proceedings of an international conference on industrial applications of magnetic separation, 1979.
- (j) International Symposium on Advances in Magnetic Filtration, 1982.
- (k) "Magnetic Separations Near Market Breakthrough," Chemical and Engineering News, 1974.



Source: NTiS-PB 275 287

Figure 47. Schematic representation of high-gradient magnetic separation for liquid streams.



3.5.10 Washout.

3.5.10.1 Description. Washout (see Figure 48) has been used at many installations for demilitarization of conventional munitions. Washout consists of jetting hot water into ammunition casings to melt and wash out the explosive fill. Both water and explosives are reclaimed. In a typical washout operation, hot water $(180^{\circ}$ to 205° F) under pressure $(90-125 \text{ psi})^{\circ}$ is injected into the casings.

The molten explosive-water slurry flows to a settling tank where most of the water is separated (gravity or dissolved air flotation) for reuse. The molten explosive is pelletized by showering droplets forced through a perforated plate and through ambient cold water, and the solidified pellets are collected, dried, and boxed for reuse. The recycle water is chilled to remove excess dissolved explosive, filtered (diatomaceous earth, mixed media, fiber filter, etc.), and sent to a holding tank for eventual feedback to the heating units.

In most cases, no water is discharged from a washout plant while it is running. Instead, treated (i.e., chilled and filtered) water is continuously recycled to the washout section and is discharged only during shutdown. The treated (chilled and filtered) water is usually passed through a carbon adsorption system to remove dissolved organics prior to reuse elsewhere or discharge to evaporation ponds, surface waters, etc.

3.5.10.2 Applicability.

- (a) Hot water washes have been used to remove and desensitize deposits of DNT, RDX, nitrocellulose, and other explosives from contaminated buildings and equipment.
- (b) This process is suitable for the removal of TNT, "Composition B" (TNT, RDX, wax), and Tritonal (TNT, Al) from ammunition casings and for subsequent recovery of these compounds and water.
- (c) Treatment of contaminated soils by washout has not been demonstrated.
- (d) Steam cleaning has been used to clean buildings and equipment contaminated by explosives.

aHigh-pressure (5,000 to 9,000 psi) systems have recently been developed for use at selected installations. Water temperatures are ambient.



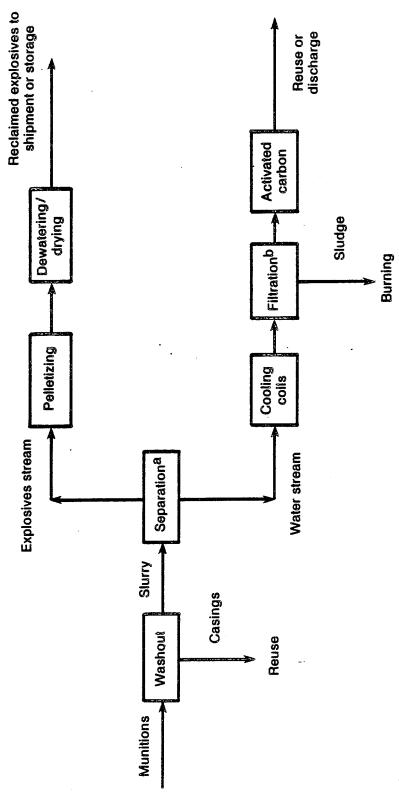
(e) An acetone/steam mixture has been suggested because explosives are soluble in acetone.

3.5.10.3 Comments.

- (a) Steam and hot-water washout produce distillation and vapor carry-over of the organic energetic materials (TNT, Tritonal, etc.), resulting in air emissions.
- (b) The sludge remaining from water discharge and evaporation on land (leaching beds) and from the water filters is normally disposed of by open burning, resulting in additional emissions.
- (c) Sludge from weekly maintenance and cleaning is also open burned.
- (d) Casings are "flashed" by open burning to remove all traces of explosives.
- (e) No information has been provided on the quantity and quality of air emissions from a washout plant.

3.5.10.4 References.

(a) Shapira et al., 1977.



a Gravity separation or air flotation. b Diatomaceous earth, fiber filters, mixed media.

Figure 48. Typical washout system for demilitarization of conventional munitions.

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- 4. TECHNOLOGY ASSESSMENT FOR RESEARCH AND DEVELOPMENT
- 4.1 The assessment process. The technologies identified and characterized in Section 3 were subjected to a two-level assessment within the context of the logic diagrammed on Figure 49. The information used in making the assessment included the following:
 - (a) Typical mixtures of the soil contaminants that were previously identified on the DARCOM installations studied.
 - (b) The status of soil contaminant regulations reported in Section 2.
 - (c) Performance, operation, and use information for specific technologies identified by the search procedures detailed in Section 3.

Execution of the assessment procedure identified technologies and unit processes that appear promising for solving various soil contamination problems identified under the USATHAMA Installation Restoration Program. Promising technologies were grouped into the following two broad categories:

- (a) Those which appeared to be applicable or adaptable in the short term.
- (b) Those which could be ready for full-scale application by FY 1987, but which require additional research, development, and testing.

For the purposes of this discussion, a number of terms have been used that require explanation. The calendar time required for bringing a specific technology from its current status for soil treatment to full-scale utilization has been called the time-to-commercialization. Fast-track technologies are considered limited research targets. They are called fast-track technologies in a time-to-commercialization context because the time to move them from their current status to full-scale utilization is relatively short. They are called limited research targets because the number of tests and experimental evaluations required for movement to full-scale are limited. Medium-track technologies are considered unlimited research targets. Medium track is used to describe the anticipated calendar time required for moving the technology from current status to full-scale utilization. This time frame is between one and four years. These same technologies are called unlimited research targets because there remain a large number of unanswered questions concerning

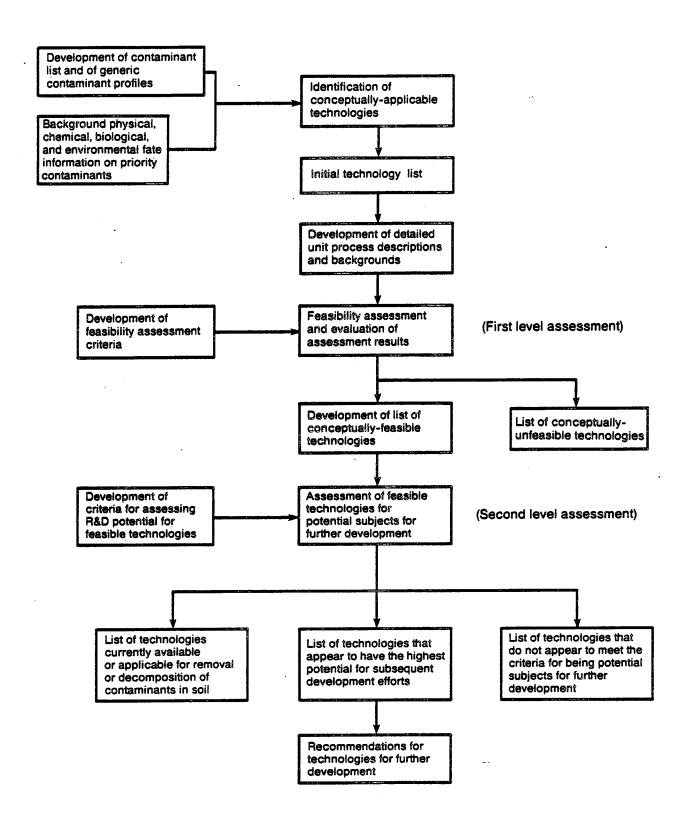


Figure 49. Work flow diagram for identification, assessment, and selection of technologies (unit processes) showing the highest potential for topics for research and development for removal or decomposition of contaminants of interest in soil.



them, and there is a potential for unlimited numbers of investigations. This may be a threat in the absence of well-designed protocols and clear definitions of objectives and goals.

Soil decontamination is a phrase of convenience and sometimes leads to confusion because of significantly different meanings applied by different groups within the Department of the Army. For this project, soil decontamination means the removal or decomposition to nontoxic or nonhazardous by-products of the identified contaminants. The phrase does not refer to radiological decontamination procedures nor to reduction of chemical or biological agent threats for this project.

4.2 First-level assessment criteria.

- 4.2.1 Purpose of first-level assessment. Technologies selected in the identification portion of this study were first assessed on their applicability for soil decontamination. Technologies were evaluated using criteria developed from environmental engineering practices and USATHAMA requirements. First-level criteria were as follows:
 - (a) Technology performance.

(b) Versatility.

- (c) Incremental residual volume.
- (d) Additional treatment requirements.
- (e) Intermedia transport.
- (f) Safety.
- (g) Area or volume limitations.
- (h) Future land use.
- (i) Contaminant interferences.
- (j) Mobility and transportability.

This phase of the assessment determined the apparent technical feasibility of a technology in either concept or practice.

Each criterion had a three-unit assessment system (+, 0, -), with "+" being very favorable and "-" being very unfavorable. The three units for each criterion had a specific definition to guide persons involved in the assessment. Definitions are listed in Table 8. First-level assessment rated technologies on their own merit. It did not attempt to rank technologies. The assessment was performed by a panel of chemical and environmental engineers selected by the project team and assisted by hydrologists and chemists.

FIRST-LEVEL ASSESSMENT CRITTERIA FOR EVALUATION OF TECHNOLOGIES POTENTIALLY APPLICABLE TO REMOVAL OR DECOMPOSITION OF SOIL CONTAMINANTS REPORTED FOR SELECTED DARCOM INSTALLATIONS TABLE 8.

Criteria	+	0	
Technology performance	Demonstrated decomposition or semoval of identified soil contaminants (e.g., explosives-related organics, heavy metals, solvents, PCB's, and pesticides) to accepted levels.	Expected but not demonstrated de- composition or removal of identi- fied soil contaminants.	Minimal demonstrated or expected decomposition or removal of identified soil contaminants.
Versatility	Demonstrated to decompose or remove both organic and inorganic contaminants of interest from soil.	Expected but not demonstrated decomposition or removal of both organic and inorganic contaminants of interest.	Expected or demonstrated inability to decompose or remove both organic and inorganic contaminants of interest from soil.
Incremental residual volume	No additional residual volume generated.	Residual volume significantly less than volume of treated soil.	Residual volume equal to or greater than the volume of treated soil.
Additional treatment re- quirements	No additional treatment require- ments.	Additional treatment for nontoxic or nonhazardous compounds required (e.g., effluent, gas scrubbing for particulate removal).	Additional treatment for toxic or hazardous compounds required.
Intermedia transport	Demonstrated minimization of transport of contaminants between environmental media (i.e., air, water, and soil).	Unproven effects on intermedia transport.	Demonstrated assistance to the transport of contaminants between media.
Safety	No demonstrated hazard to workers or local residents during or after application.	Hazardous materials contained or controlled with minimum threat to workers or local residents during or after application.	Demonstrated or strongly suspected hazards to workers or local residents during or after application.
Area or volume limitations	Demonstrated ability to process large areas or large volumes of contaminated soil.	Adaptability to process large areas or large volumes of contaminated soil.	Demonstrated or expected limita- tions on the area or volume of soil that can be processed.
Future land use	Original contaminated site will have unrestricted public use af- ter application.	Original contaminated site will have limited public use after application (e.g., industrial use).	Original contaminated site will be greatly restricted in use or access after application.
Contaminant interferences	Demonstrated to be unaffected by the presence of other contami- nants of interest.	Not expected to be affected by the presence of other contami- nants of interest.	Expected to be adversely affected by the presence of other contaminants of interest.
Mobility and transporta- bility	Demonstrated to be easily transported between sites.	Expected to be adaptable for transport between sites.	Not transportable between sites.



4.2.2 First-level assessment criteria.

- 4.2.2.1 Technology performance. This criterion assessed a technology's ability to remove or decompose the specific soil contaminants identified. Technologies with demonstrated effectiveness against any number of the contaminants of interest were rated high. Technologies with demonstrated ineffectiveness were rated low. This criterion was applied using best engineering judgment since quantified performance standards were not available at the time of the analysis.
- 4.2.2.2 Versatility. The contaminated soils analyzed in Section 2 had contamination profiles featuring both heavy metals, and organic compounds. This criterion rated the ability of a technology to successfully decontaminate both organics and inorganics. This criterion did not attempt to rate possible contaminant interferences with the performance of a technology.
- 4.2.2.3 Incremental residual volume. Sometimes the volume of residuals produced by a technology is greater than the original contaminated volume. This creates a disposal problem. This criterion rated a technology on its ability to reduce the volume of the residual material.
- 4.2.2.4 Additional treatment requirements. Soil treatment technologies, while removing contaminants from soils, might produce residuals that must be processed. The treatment or disposal of residuals may be more costly than the initial soil treatment. This criterion scores each technology on its ability to produce nontoxic residuals. Systems that produce toxic residuals requiring further treatment will rate poorly by this criterion.
- 4.2.2.5 Intermedia transport. It is possible that a decontamination process may alter the ambient conditions of the site. This may cause the movement of otherwise immobile contaminants to other media. This could have adverse effects on the local population, especially if groundwater is contaminated. This criterion rates a technology on its ability to minimize the spread of soil contaminants to other environmental media.
- 4.2.2.6 Safety. It is possible that the operation of soil decontamination machinery or the application of a specific unit process may create unsafe conditions for the operators or for local residents. This criterion evaluates a technology on its inherent safety implications for workers and local residents.



- 4.2.2.7 Area or volume limitations. Since the volume of soils at contaminated sites is often very large, a removal process should be able to destroy contaminants at an efficient rate. This criterion rates each technology on its ability to decontaminate large volumes of soil within a reasonable timeframe.
- 4.2.2.8 Future land use. It is the goal of any decontamination technology to render a once contaminated site safe for unlimited use. This criterion attempts to anticipate the results of the application of a technology to a given site. Sites that will be able to have unlimited public use upon completion of the contaminant removal process will rate high in this category.
- 4.2.2.9 Contaminant interferences. Contaminated sites of interest often contain both organic and inorganic contaminants. It is possible that a process to remove organics will not perform to its capability due to the presence of inorganics and vice versa. This criterion rates each technology on its ability to perform in the presence of many contaminants.
- 4.2.2.10 Mobility and transportability. A technology that can be designed to be modular or trailer mounted is very attractive to the end user. Multiple sites can be serviced by the same hardware system. This criterion rates the potential for the modular, transportable design of a system using the technology in question.
- 4.2.3 First-level assessment procedure. The individuals who participated in the first-level assessment received a package that contained the technology descriptions presented in Section 3, ballots (as shown in Appendix B), and the assessment key shown in Table 8. Each technology was presented verbally by the project engineers to the assessment team. This presentation was followed by discussions and completion of the assessment ballots. Votes were encouraged to be accompanied by explanatory comments.

After the ballots were completed, they were collected and tabulated. One vote (either +, 0, or -) was selected for each criterion for each technology based on a majority vote for a particular criterion. When a large disparity of votes occurred (i.e., 2:+, 2:0 and 2:-), the comments were used to resolve the situation. (The comments enabled the tabulator to identify and resolve misunderstandings.) The tabulated summary results are presented in Tablés 9 through 12.

TABLE 9. FIRST-LEVEL EVALUATION SUMMARY RESULTS: THERMAL TECHNOLOGIES (Evaluation ratings of "0" are shown as blanks for clarity)

Technology	Perform- ance	Versa- tility	incre- mental residual	Addi- tional treat- ment	Inter- media trans- port	Safety	Area or volume limits	Future land use	Contam- inant inter- ferences	Mobility or transport- ability
Vertical well chemical reactor		ı		1	+	+				
Multiple hearth incinerator	+	,					+		+	
Rotary kiln incinerator	+	,					+		+	+
Molten salt incinerator		ı							+	
Wet air oxidation		1		ı	+				+	
In-situ vitrification	+	+	+	+		1			+	
Plasma arc torch	+	+					ı		+	
Microwave plasma detoxification	+							+	+	
Burning/torching	•	1			,	1	ı		+	+
Hot air/steam stripping		ı		ı	ı	t	1		+	1
Low temperature thermal decomposition +	ion +	1				+			+	
Supercritical water oxidation							ı	+	+	
Fluidized bed incineration	+	t							+	
High temperature fluid wall	+	+	+			+			+	
Laser-initiated thermal decomposition	ion	•								, +

TABLE 10. FIRST-LEVEL EVALUATION SUMMARY RESULTS: CHEMICAL TECHNOLOGIES (Evaluation ratings of "0" are shown as blanks for clarity)

Pe	Perform- ance	Versa- tility	Incre- mental residual	Addi- tional treat- ment	Inter- media trans- port	Safety	Area or volume limits	Future land use	Contam- inant inter- ferences	Mobility or transport- ability
Sulfur-based reduction (in-situ)	+			ı	•	_		0		
Sulfur-based reduction (on-site)	+			1						
Enercol oxidation process		,					•			
Solvent extaction (in-situ)	+	+		ŧ	ı	ı	+			+
Solvent extraction (on-site)	+	+		ŧ	+	1	*	+		+
Free radical oxidation	+	•	.		+		ı			
Decontamination of soils with Franklin solvent		- 1	•	+		+				
Carbon adsorption	+ .	9	ı	9		+			ı	+
Ion exchange	+	1	ı	,			•		1	+
Surfactant complexing	+	;		ı		+		+		
Solvent extraction (Acurex process)	+	ı			+	+	+	+		+
Removal of metals using dithiocar- bamate		:		i	+	+	ı		•	•
Philadelphia Quartz (PQ) method for removing heavy metals		ı			+	+	ı			
Removal of heavy metals using cellulose xanthate		•		•		+	t			
Fenton reagent (in-situ)	+	•			•	+		ı		
Penton reagent (on-site)	+	t				+				
Base-initiated decomposition (insitiu)	+	ı			t	+		ı		
Base-initiated decomposition (on-	+	ı				+				·
Chemical reduction with sodium borohydride	+			1						

J

TABLE 11. FIRST-LEVEL EVALUATION SUMMARY RESULTS: BIOLOGICAL TECHNOLOGIES (Evaluation ratings of "0" are shown as blanks for clarity)

Pechnology	Perform- ance	Versa- tility	Incre- mental residual	Addi- tional treat- ment	Inter- media trans- port	Safety	Area or volume limits	Future land use	Contam- inant inter- ferences	Mobility or transport- ability
Microbial bioaccumulation		\$		1		+	ı			
Immobilized cells	ı	1				+	ı	i	1	
Vermicomposting		ı		+		+		•		
Composting	+	1		+						
Aerobic biodegradation		1			+	+	ı		1	
Biodegradation with adapted microbes		ı			+	+			ı	
Anaerobic biodegradation		ı				+	· •			ŧ
Vegetative uptake	+	1		ı		+				•
Landfarming		i	+	+		+				1 -
Bioreclamation of solids (GDS process)	+	1			ı	+				ı
Fluidized bed biological treatment		•				+	ı			
Anaerobic/aerobic cycling						+				

TABLE 12. FIRST-LEVEL EVALUATION SUMMARY RESULTS: PHYSICAL TECHNOLOGIES (Evaluation ratings of "0" are shown as blanks for clarity)

Technology	Perform- ance	Versa- tility	Incre- mental residual	Addi- tional treat-	Inter- media trans- port	Safety	Area or volume limits	Future land use	Contam- inant inter- ferences	Mobility or transport- ability
Secured landfill	+	+	+		+		+	+	+	
Slurry wall				t		+	+	ı		+
Grouting	1			,		+	÷	1	+	+
Geological isolation		+	+	+			9	+	+	•
Microencapsulation	+		1			1		+		+
Macroencapsulation	+					ı		+		+
Stabilization			G	ı		,	+			+
High gradient magnetic separation		. 1				+		+	+	
Washout		•	•	1			1		+	



- 4.2.4 Analysis of first-level assessment. Once tabulated, all the pluses and minuses were added for each technology by assigning a +1 score to a + and a -1 to a -. A technology receiving more pluses than minuses was considered to be potentially or conceptually feasible for soil contamination. Feasible technologies are discussed in the paragraphs that follow.
- 4.2.4.1 Thermal processes. Ratings ranged from a high of +5 for the high temperature fluid wall reactor to a low of -5 for hot air/steam stripping.

The multiple hearth incinerator (+2) and rotary kiln (+3) rated high in technology performance, incremental residual volumes, and contaminant interferences. These processes have been demonstrated to remove organics from waste streams. Inorganics present in the waste stream should not affect the operation of these incinerators, and each incineration system can be designed for large throughputs. A trailer-mounted rotary kiln pilot unit has been put in use by EPA. A different transportable rotary kiln pilot unit is being tested for decontamination of explosives-laden sediments under Task 2, Contract No. DAAK11-82-C-0017.

The molten salt (0) and fluidized bed (+1) incinerators did not rate as well. There were questions concerning their ability to handle large throughputs. The molten salt incinerator's performance was also rated low. Full-scale data were not available for a mix of contaminants analogous to those of interest.

All incinerators were given a minus in versatility since the technology addresses organic contaminants but not inorganics. Heavy metals will not be affected at typical operating temperatures of $1,500-2,000^{\circ}F$.

High temperature thermal destruction processes were rated favorably. These included in-situ vitrification, +4; high temperature fluid wall, +5; plasma torch, +2; microwave plasma, +3. These processes operate at temperatures above 3,000°F, in which organics are destroyed. Heavy metals can be fixed in a vitrified matrix.

The vertical well chemical reactor and wet air oxidation are organic removal processes that produce an effluent stream of low molecular weight organics. Incomplete destruction of organics resulted in ratings of 0.



Low temperature thermal processes (+2) have been successful in removing organics from waste streams under laboratory conditions. These processes were not disrupted by inorganics present and appeared to meet reasonable safety criteria.

Supercritical water oxidation (+1) is a developmental process with limited laboratory data. No contaminant interferences are anticipated. If the process is operated to potential, it will oxidize organics and precipitate inorganics.

Laser-initiated thermal decomposition (-1) is an organics removal process that is in the developmental stage. Current information indicated limited versatility and restrictions on throughput.

Remaining processes in this category showed few advantages when applied to removing contaminants from soils and were rated very low. Burning/torching received a -2, and hot air/steam stripping receiving a -5.

4.2.4.2 Chemical processes. Ratings ranged from +5 to -3. In general, on-site processes consistently rated higher than insitu processes. This resulted from ratings on intermedia transport and future land use after treatment.

Solvent extraction processes, both generic and the proprietary Acurex process, were rated high on the basis of their performance, versatility, and transportability. Reduction processes (sulfur based, sodium borohydride) rated 0-2 for in-situ treatment and 0 for on-site treatment. The application of these technologies requires additional treatment of the process residuals since these processes rely on precipitation as the mechanism of contaminant removal.

Metal-complexing processes (dithiocarbamate, the Philadel-phia Quartz complexing agent, and cellulose xanthate) rely on precipitation of metals as the removal mechanism. This requires additional treatment for a process residual solid waste stream. As a result, these technologies were rated -1 or -2.

Surfactant complexing of organics (+1) was rated higher than those just mentioned since it has been used on soils contaminated with organics with some success. The process is also inherently safe and was rated high in future land use.



On-site chemical oxidation processes (free radical, Fenton, base initiated) have been demonstrated for destruction of many organics. These processes exhibited good safety qualities, and on-site use did not appear to promote movement of contaminants into other media. These facts resulted in ratings of +1 for on-site.

The Enercol oxidation process (-2) was rated low because the information available did not answer questions concerning process capacity and versatility.

Carbon adsorption and ion exchange appeared to have little application to the solid phase.

- 4.2.4.3 Biological processes. Ratings ranged from +1 for composting, vermicomposting, and landfarming to -4 for immobilized cells. All biological processes received poor ratings in versatility since they attack only organic contaminants. All biological processes received high ratings in safety. They received low ratings in area or volume limits and mobility.
- 4.2.4.4 Physical processes. Ratings ranged from +6 for secure landfill to -3 for washout.

The secure landfill (+6) is a state-of-the-art technology used for solid waste disposal of a wide variety of toxic and hazardous materials. Off-site landfilling permits unrestricted use of the originally contaminated site.

Geological isolation (+3) has many characteristics exhibited by secure landfill.

Fixation/stabilization technologies received ratings of +1 to -1. Encapsulation processes were rated higher because they appeared to effectively remove contaminants from the general environment.

Grouting (+1) and slurry wall (0) technologies only serve to isolate contaminants. Without further processing, the contaminated site will have restricted use.

Magnetic separation (+2), although applicable only to metallic and paramagnetic compounds, has safe operating conditions and is minimally affected by organic contaminants.



4.2.5 Criteria for advancement to the second level. The first-level assessment was a filter for conceptual feasibility. Technologies that did not appear to be applicable or adaptable to remove or decompose the contaminants of interest from soil were eliminated. Those that survived this elimination process were subjected to closer scrutiny. If a technology had an overall positive evaluation from the first-level assessment but had unfavorable ratings in either performance or future land use, it was also eliminated. The technologies and unit processes that were judged to be conceptually feasible are listed in Table 13.



TABLE 13. TECHNOLOGIES JUDGED TO BE CONCEPTUALLY FEASIBLE FOR REMOVAL OR DECOMPOSITION OF SOIL CONTAMINANTS OF INTEREST

1. Thermal processes

In-situ vitrification
High temperature fluid wall
Rotary kiln incinerator
Microwave plasma
Low temperature thermal
Multiple hearth incinerator
Plasma arc torch
Super critical water oxidation
Fluidized bed incineration

2. Chemical processes

Solvent extraction (Acurex process)
On-site solvent extraction
Free radical oxidation
In-situ solvent extraction
Soil decontamination using the Franklin solvent
Surfactant complexing
Fenton reagent
On-site base-initiated reduction

3. Biological processes

Composting Vermicomposting Landfarming

4. Physical processes

Secure landfill Geological isolation Macroencapsulation Magnetic separation Microencapsulation



4.3 Second-level assessment.

- 4.3.1 Purpose. The second level of the assessment process had the following objectives:
 - (a) Discriminate between technologies that are commercially available and those that are developmental or conceptual.

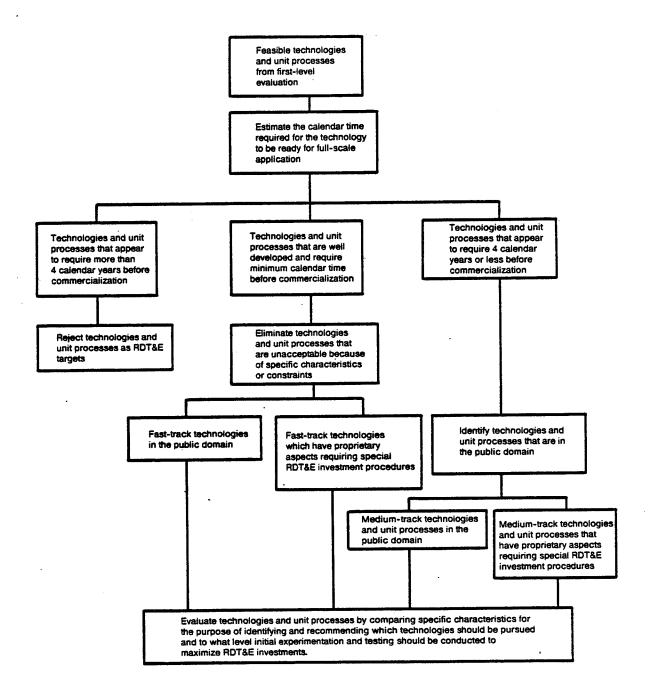
(b) Identify technologies that are worth further research and development investments.

It is assumed that USATHAMA does not wish to compete with private developers or infringe on patent (or patent pending) rights.

With these objectives in mind, the criteria discussed in the subsection that follows have been developed to complete the second level of technology assessment. The procedure that was used during the second-level evaluation is shown on Figure 50.

4.3.2 Second-level assessment criteria.

- 4.3.2.1 Time to commercialization. A critical programmatic goal expressed by USATHAMA was to implement new technologies for the Installation Restoration Program no later than FY 1987. This criterion differentiated between those technologies that are presently commercialized for removal of contaminants from soils, those technologies that are anticipated to be ready for commercialization by FY 1987, and those technologies that will not be commercialized by FY 1987.
- 4.3.2.2 Proprietary status. This criterion differentiated between those technologies that are in the public domain (+) and those for which there are important or restricting proprietary aspects (-). The reason this criterion was included rested on perceptions of differences in R&D investment procedures that were dependent on whether a technology was public or private property.
- 4.3.2.3 Estimated relative commercialization cost. In general, all of the technologies identified as conceptually feasible would require some level of RDT&E investment before they were ready for full-scale implementation at specific sites. This criterion was a judgmental evaluation of the level of RDT&E investment required to bring a specific technology from its present level of development to full-scale implementation.



Note: The purpose of this procedure was to identify technologies or unit processes that were judged to be conceptually feasible from the first-level evaluation and appeared to have promise as research or development targets.

Figure 50. Second-level technology evaluation procedure.



- 4.3.2.4 Estimated relative operational costs. These costs are difficult to quantify at this time since there was not enough information available. This criterion was a best estimate of operational costs using a secure landfill as the basis for comparison.
- 4.3.2.5 Environmental impact. The application of a technology to a contaminated site will always have some effect on the ecology of the area. This criterion assessed the ability of a contaminated site to recover after the application of a technology.
- 4.3.2.6 Unit process interactions. Many times removal technologies are contaminant specific; i.e., the technology may be able to remove only a select group of solvents. Given the contamination profiles developed in Section 2, it may be necessary to employ several technologies to remove all of the contaminants present at a site. This criterion assessed the ability of each process to either stand alone or be easily linked with other unit processes.
- 4.3.2.7 Versatility. This criterion is a repeat from the first-level assessment. It was used in the second-level assessment to further point out the ability of technologies to remove both organics and inorganics from contaminated soils.
- 4.3.2.8 Questions for consideration. In addition to the set of evaluation criteria just listed, four questions on topics warranting further consideration were included. The questions were not discriminatory in the sense that technologies would survive or fail second-level assessment, but they were felt to be relevant to final recommendations on R&D investments. The questions are listed on the bottom of Figure B-2.
- 4.3.3 Second-level assessment process. A second-level evaluation was conducted according to the logic flow on Figure 50. Technologies selected for second-level assessment were rated against the seven criteria and four nondiscriminatory questions detailed in the previous subsection. Table 14 details the criteria evaluation levels. Summary ratings are presented on Figure 51.

The logic diagram, shown on Figure 50, indicates that the time required to bring a given technology to full-scale implementation was the most important discriminator in the second-level assessment. Technologies or unit processes that required more than four calendar years for commercialization were eliminated from further consideration. Technologies meeting the time

TABLE 14. SECOND-LEVEL EVALUATION CRITERIA

Criteria	+	0	•
Time to commercialization	Commercialized or can be immediately adapted for removal or decomposition of soil contaminants of interest.	Expected to be commercialized for removal or decomposition of soil contaminants of interest by FY 1987.	Unlikely to be commercialized by PY 1987.
Proprietary status	In the public domain.	In the public domain, but proprietary variations exist.	Proprietary.
Estimated relative commercialization cost	RDIGE cost is comfortably within the budget.	Cost might strain the budget.	RDTEE cost expected to exceed reasonable budget constraints.
Estimated relative operational costs	Less than disposal in an off-site secure land-fill.	Approximately equal to disposal in an off-site secure landfill.	Significantly greater than disposal in an off-site secure landfill.
Environmental impact	Impact during application is insignificant or within reasonable limits, with complete ecological recovery after application.	Adverse impact during application with full ecological recovery expected after application.	Significant adverse impact during application with only partial ecological recovery expected after application.
Unit process interactions	Either stand-alone or easily linked with other unit processes.	Unknown capability to be linked with other unit processes.	Cannot be easily linked with other unit processes for development of a system; linkable only in disjointed or discontinuous systems.
Versatility	Demonstrated to decompose or remove both organic and inorganic contaminants of interest from soil.	Expected but not demonstrated decomposition or removal of both organic and inorganic contaminants of interest.	Expected or demonstrated inabil- ity to decompose or remove both organic and inorganic contami- nants of interest from soil.
Considerations that do not comprise discriminatory	t comprise discriminatory evaluation criteria:	Yes No	

Is process equipment, hardware, software, or a demonstration system currently available for field demonstration or pilot-scale testing?

Can reliability be designed into the hardware/software subsystems without exorbitant expense?

Are exotic or strategic materials required? ۳. Are there materials handling risks to be assessed?

Technology	Time to commercialization	Proprietary status	Estimated relative commercialization cost	Estimated relative operational cost	Environmental impact	Unit process interaction	Versatility
Secure landfill	1	+	+			+	+
Solvent extraction- acurex process		•				+	•
On-site solvent extraction		+	+			+	+
In-situ vitrification		•			•	+	+
High temperature fluid wall		+		•		+	+
Rotary kiln incinerator	*		+	•		+	•
Geological isolation		+	•	•		+	+
Microwave plasma				•		*	
Low temperature thermal degradation on all in-situ	*	+	*	•		+	•
Multiple hearth incinerator	•			•		+	•
Macroencapsulation	· +		+	•		+	•
Magnetic separation				•		+	
Free radical oxidation (on-site)		+		•		+	•
In-situ solvent extraction		+	+		•	+	
Decontamination using franklin solvent		•	+			+	•
Surfactant complexing		+		+		+	•
Microencapsulation	+		+	•		+	
Composting	+	+	+			+	•
Vermicomposting	+	+	+			+	•
Landfarming	+	+	+			•	-
Plasma arc torch				•		+	+
Super critical water oxidation				•		• .	
Fluidized bed incinerator	+			•		+	•
Fenton's reagent (on-site)		+	+	•		+	•
Base-initiated reduction (on-site)		+	+ •	•		*	-

Figure 51. Summary of second-level assessment. (Evaluation ratings of "0" are shown as blanks for clarity)



to commercialization criterion were given further evaluation. Ultimately, it was desired to identify technologies that could be fielded within a minimum time-frame (fast track), or that could be fielded within the four-year time constraint (medium track).

Second-level evaluations were made on the basis of information used for first-level evaluations and new information obtained between evaluations. Once the evaluation forms were completed, the technology ratings for each criterion were compiled. Any disputes were resolved by referring to the evaluators comments that accompanied each rating.

4.3.4 Analysis of second-level assessment. It was important to first identify technologies as those ready for commercialization now, those that may be ready by FY 1987, and those that will not be ready for commercialization by FY 1987.

The conceptual framework for categorizing technologies according to time-to-commercialization is shown graphically on Figure 52. This figure shows the conceptual schedule for taking a given technology from bench-scale experimentation through design, fabrication, installation, and shakedown of a full-scale system.

Technologies already commercialized or readily adaptable full-scale to DARCOM soil contamination problems were recognized as requiring a limited amount of R&D. These technologies were identified as limited research targets in the sense of requiring the least amount of developmental work prior to full-scale implementation, and they were called fast-track targets on the basis of minimum calendar time required before full-scale utilization. Technologies falling into this category were considered to be appropriate subjects for site-specific treatability studies, site-specific economic analysis, limited demonstration experimentation, or full-scale design on the basis of existing and limited new information. These technologies were rated "+" during second-level assessment.

Technologies receiving a "0" rating should be able, based on best engineering judgment, to fit into the development schedule pictured on Figure 52. Some of the technologies receiving a 0 rating may have already been through the early stages of the development cycle. Technologies rated as "-" would not be ready for commercialization by FY 1987 and received no further consideration.

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Note: The base of each triangle denotes the anticipated calendar time required for initiating each development activity. The peak of each triangle denotes the anticipated start of engineering work in contrast to administrative work.

Figure 52. Development time frame within which technology evaluations were made.



Summary results of the second-level assessment for short-, medium-, and long-range R&D targets are presented in Table 15. The nine technologies designated as limited research targets are those technologies that require the least number of experimental tests and evaluations before being implemented full-scale. The 15 technologies listed in Table 15 that are designated as unlimited research targets are those that require a relatively large number of tests and evaluations before full-scale design is reliable. However, these tests can be accomplished in the four-year time constraint with a reasonable effort. The one technology listed in Table 15 as a long-term research target, supercritical water oxidation, was perceived to require more than four years to reach full-scale implementation.

Second-level assessment to this point was conducted using a set of criteria common to all of the technologies evaluated. Each technology was evaluated on its own merits without reference or comparison with other technologies. From this point, second-level assessment continued by considering technical and other constraints that were, for the most part, peculiar to specific technologies.

The limited research target technologies listed in Table 15 were subsequently evaluated according to the logic diagram shown on Figure 53. For a number of reasons, it was recognized that some technologies in this category were simply not acceptable to the Department of the Army as actual topics for RDT&E investment. The secure landfill was a case in point. Of the technologies that were acceptable RDT&E targets, some were already under study; rotary kiln incineration was an example. Technologies currently under study were not considered valid topics for further consideration under this project because the costs of those studies were perceived as sunk costs, and new information to be obtained from those studies would certainly influence decisions on subsequent efforts.

Acceptable RDT&E topics not currently under study became potential RDT&E projects. Of those, some were perceived to be redundant in the sense that information already on hand or to be obtained from current projects would also be developed by redundant projects. Incineration methods other than rotary kiln were examples. Redundant potential projects were rejected as target potential projects.



TABLE 15. PRELIMINARY RESULTS OF SECOND-LEVEL ASSESSMENT

1. Limited research targets

Secure landfill
Rotary kiln incinerator
Multiple hearth incinerator
Microencapsulation
Macroencapsulation
Landfarming
Fluidized bed incineration
Composting
Vermicomposting

2. Unlimited research targets

Geological isolation
On-site solvent extraction
Surfactant complexing
Fenton reagent
Base-initiated reduction
Free radical oxidation
In-situ solvent extraction
Low temperature thermal decomposition
Solvent extraction: Acurex process
In-situ vitrification
High temperature fluid wall reactor
Microwave plasma
High gradient magnetic separation
Plasma arc torch
Decontamination of soils using the Franklin solvent

Long-term research targets

Supercritical water oxidation

Note: Limited research targets are those technologies that might be placed on a fast-track program for site-specific full-scale implementation because only a limited amount of testing and evaluation is required.

Unlimited research targets are those technologies that might be placed on a medium-track program because a larger amount of new information on performance and design is required. These technologies may require all four stages of development as shown on Figure 52.

Long-term research targets are those that need more than four years for full-scale implementation.

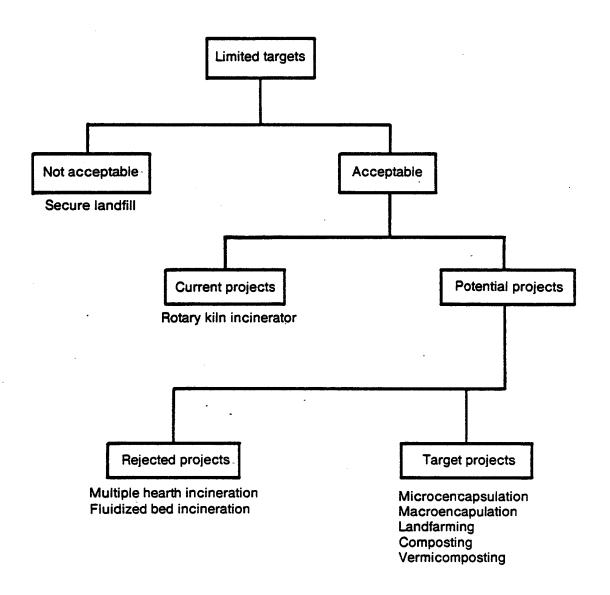


Figure 53. Categorization process for identifying limited R&D targets.



The result of this analysis indicated that topics for consideration in the fast-track, limited research target category were as follows:

- (a) Microencapsulation.
- (b) Macroencapsulation.
- (c) Landfarming.
- (d) Composting.
- (e) Vermicomposting.

In a similar manner, technologies requiring more detailed and broader studies within the four-year development time constraint were analyzed according to the logic diagram shown on Figure 54. Technologies that were unacceptable to the Department of the Army for any reason were segregated first. Topics that were acceptable but that were currently under study were identified and segregated next. Potential RDT&E topics were classified according to whether they fell within the public domain or were proprietary in some sense. For example, some technologies were generic in concept but proprietary in available pilot-scale equipment. Both public domain and proprietary technologies were considered valid RDT&E targets, but the investment procedures for each would likely differ.

The results of this analysis indicated that public domain technologies that would be potential RDT&E topics were the following:

- (a) Free radical oxidation.
- (b) In-situ solvent extraction.

Proprietary technologies that would be potential mediumtrack RDT&E topics were the following:

- (a) Acurex solvent extraction process.
- (b) In-situ vitrification.
- (c) High temperature fluid wall reactor.
- (d) Microwave plasma reactor.
- (e) High gradient magnetic separation.
- (f) Plasma arc torch.
- (g) Chemical decomposition using the Franklin solvent.

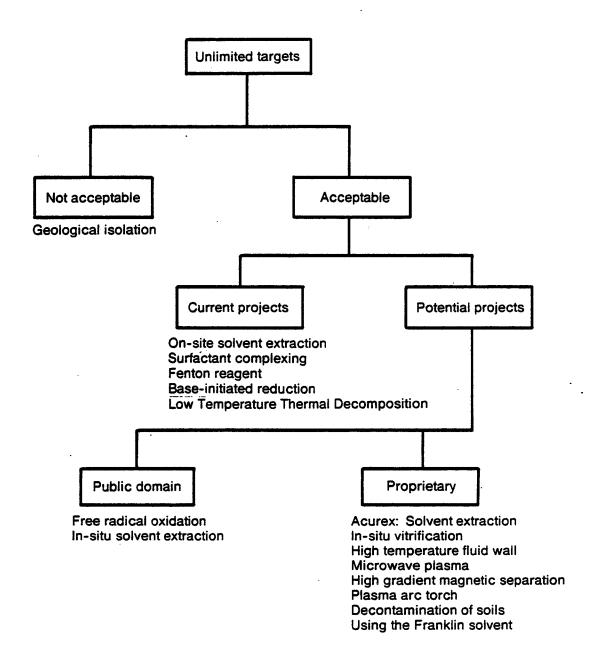


Figure 54. Categorization process for identifying unlimited R&D targets.



5. DISCUSSION, FINDINGS, AND RECOMMENDATIONS

5.1 <u>Discussion</u>. Fifteen technologies were identified as possible RDT&E topics (see Figures 53 and 54). All 15 could be actual topics of investigation starting in FY 1984. However, such a program would most likely dilute limited resources and delay payoff beyond acceptable limits. Instead, there were additional considerations brought forward during the second-level assessment that worked toward defining a more limited list of topics that appeared to better fit time/budget constraints.

The typical contaminant profiles indicated that most of the sites of interest have a mixture of organic and inorganic contaminants. Therefore, technologies that are effective for both types of compounds without the need for additional treatment might be more attractive than technologies that must be linked into treatment systems.

Land use after remedial action is important. Technologies that permit unlimited post-remedial action land use were considered more attractive than technologies of superlative performance, but which created restricted land use after application.

The type and extent of required testing was a consideration. Some technologies need only a limited number of tests under site-specific conditions to determine if they are applicable. Other technologies have been demonstrated on subsets of the contaminants of interest, and need limited testing to determine if more general applications are possible.

Using these and related considerations, each of the 15 potential RDT&E target technologies was further evaluated. Microand macroencapsulation are the subjects of basic research under an effort parallelling this project. Although engineering studies on these technologies are not in progress, it was thought prudent to delay recommendations for or against them as engineering targets until additional information is developed in the parallel investigation.

Landfarming was considered to have the lowest priority for subsequent investigations on the basis of limited site applicability. Experience with landfarming as a soil decontamination process is limited. It appeared, however, that this technique would be a candidate for specific sites rather than for generic studies.



Composting and vermicomposting remain attractive under the right conditions. Previous investigations have been inconclusive relevant to design and performance. Decomposition of explosives under controlled conditions has been demonstrated. There appears to be merit in limiting the testing of these processes for performance and design characterization.

Free radical oxidation is a chemical process that has been found effective in the destruction of organics in a number of aqueous systems. However, there appear to be a number of problems concerning the efficiency of the process where soils are concerned. Contaminant concentrations in soils are anticipated to be relatively low compared with concentrations of other materials also amenable to oxidation. The implications of having to oxidize everything else before addressing the target organics unfavorably bias this process.

In-situ solvent extraction is an interesting concept that relies on reliable control of subsurface fluid behavior. This limits the utility of the process to sites having known, controllable hydrogeology, and reduces the attractiveness of the process as a priority R&D target.

The Acurex solvent extraction process and the Franklin solvent process were originally developed for detoxification of PCB's. How the reactants in each process affect other soil contaminants of interest is unknown. A limited set of tests are warranted to resolve these questions.

In-situ vitrification and high temperature fluid wall (HTFW) reactor are proprietary processes being developed specifically for soil decontamination. These technologies are capable of generating temperatures of 4.000° F. At these temperatures organics are thermally destroyed and inorganics are vitrified. These processes require a moderate amount of research and development to identify and evaluate design and operation parameters.

Microwave plasma detoxification is a developmental process that uses an ionized gas produced by microwave-induced electron reactions with neutral gas molecules. At this time, the equipment that exists is laboratory-scale. Scale-up of this process has been shown to be very difficult. This fact would limit its potential within USATHAMA's R&D program.



High gradient magnetic separation is a developmental process that is able to remove contaminants from waste streams using a magnetic field. Although this process has been commercialized for ore beneficiation and coal desulfurization, it is felt that the process's applicability to soil decontamination is limited to a small number of special cases.

The plasma arc torch is a developmental technology that uses an electrical charge to produce a gas plasma. The technology will thermally destroy organics and will vitrify inorganics. This device merits limited testing to determine design parameters and characterize performance.

5.2 <u>Findings</u>. Final review of potential RDT&E targets revealed that eight of the 15 technologies identified from the second-level assessment were attractive topics for further research and development. These eight technologies fell into two categories: those that warranted very limited testing, and those that warranted more extensive experimental evaluation. The two groups are shown on Figure 55.

Screening or limited evaluation testing was considered for the purpose of evaluating design parameters, determining effectiveness against soil contaminants different from those for which a technology was originally developed, verifying performance claims, or rectifying inconclusive results from previous studies. This type of testing is recommended to be short-term, well planned and controlled, and relatively low cost. Technologies that were found to warrant limited screening and evaluation testing were the following:

- (a) Plasma arc torch.
- (b) Franklin solvent process.
- (c) Acurex solvent extraction process.
- (d) Composting.
- (e) Vermicomposting.
- (f) Landfarming.

Extensive experimental evaluation testing was considered for the purpose of developing design, performance, and operational parameter information. This is a generic type of experimental project that includes the following:

- (a) Sufficient literature review to define both the process and the experimental conditions.
- (b) Development of empirical models for design and operation.

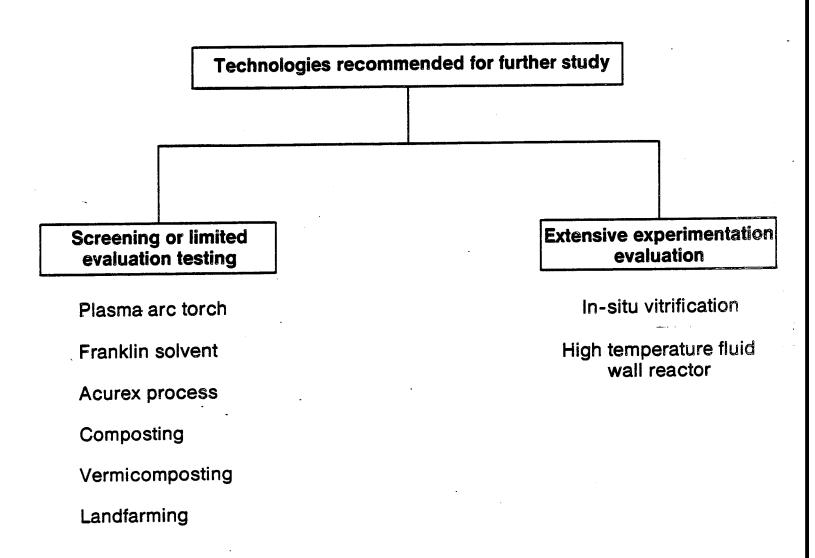


Figure 55. Technologies and types of experimental studies recommended for further consideration for the removal of contaminants from soil.



- (c) Evaluation of model parameters.
- (d) Sensitivity analyses.
- (e) Performance testing.
- (f) Scale-up conditions.
- (g) Identification and testing of intrumentation and control.
- (h) Pilot-scale demonstration at specific sites.
- (i) Full-scale design and design verification.

Technologies that were thought to warrant such a program were as follows:

- (a) In-situ vitrification.
- (b) High temperature fluid wall reactor.

Micro- and macroencapsulation were considered as candidates for screening or limited evaluation testing. It was decided to delay recommendations for or against actual testing until preliminary information from a parallel study on fixation/encapsulation mechanisms was available.

5.3 Recommendations. It is recommended that the eight technologies shown on Figure 55 be considered for the types of experimental studies shown.

The preceding recommendations resulted from analyses and evaluations based on the total scope of reported soil contaminants. Special cases were not represented. However, there is a special situation in which DARCOM has a particular interest. This is the removal of volatile compounds, particularly solvents, from soils. Additionally, DARCOM is interested in low temperature, i.e., ambient to a few hundred degrees Fahrenheit, removal technologies for this special class of contaminants. Therefore, a test plan will be developed subsequent to this report for bench-scale evaluation of low temperature removal of volatile soil contaminents.



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APPENDIX A PHYSICAL PROPERTIES

PHYSICAL PROPERTIES OF ORGANIC EXPLOSIVES AND THEIR DEGRADATION PRODUCTS TABLE A-1.

Terrance of the second

_	Compound	Structure	Formula	Molecular Weight	Specific Gravity	Melting Point (oc)	Melting Boiling Point Point (OC) (OC)	Water Solubility (in 100 part	Alcohol Solubility Solubility (in 100 parts) (in 100 parts)	Other Solvents (in 100 parts)	Vapor Pressure	Normalized Sorption Partition Coefficient Koc +	Toxicity
	2,4,6-Trinitrotoluene (TNT)	O ₂ N CI ₁₃ NO ₂	CH ₃ C ₆ H ₂ (NO ₂) ₃	227.1	1.65	18	240 expl.	.013 ²⁰ insol.	1.5 ²² sl.sol.	5 ³³ in ether V.sol. in acetone,109 ²⁰ in benzene	10 ⁻⁴ mm	900 (1) 190 (2)	Toxic effect: (anemia £ liver damage)
	2,4-Dinitrotoluene (2,4-DNT)	NO ₂	СН ₃ С ₆ Н ₃ (NO ₂) ₂	182.1	1.3271	11	300 expl. or decomp.	.03 ²² insol.	1,2 ²⁰ sl. sol.	9 ¹⁵ in ether sol, in acetone, benzene	5.1x10 ⁻³ mm 820°C	87 (3) 363 (1)	Suspected to be carcinogenic
A-	2,6 - Dinitrotoluene (2,6-DNT)	O ₂ N CH ₃ NO ₂	СН ₃ С ₆ Н ₃ (NO ₂) ₂	182.1	1.28	99	-	.001 ²⁰ insol.	sol.	Sol. in acetone, ether, benzene	.018 mm @20°C	100 (3)	Carcinogenic
1	Tetryl (nitramine; Namethyl-N,2,4,6- tetranitroaniline)	CH ₃ - N-NO ₂ O ₂ N NO ₂	02 N0 ₂ N (CH ₃) NO ₂	287.1	1.5719	131	187 expl.	.008 20 insol.	.65 ²⁰	sl. sol. in ether sol ₂₀ in acetone (75 ²⁰), benzene			Токіс
	RDX (cyclonite; Hexahydro-1,3,5- trinitro-1,3,5-triazine)	/ / z	C ₃ H ₆ N ₃ (NO ₂) ₃	222.1	1.82	205	expl.	.005 ³⁰ insol.	.105 ²⁰ insol.	ellsol. in ethor acetone (7.30) insol. in benzene	4.1x10 ⁻⁹ mm @20°C	420 (2)	Undetermined toxicity, metabolic products may be toxic
i	имх (Cyclotelramethylene- telranitramine)	$\begin{array}{c c} O_2 N & \searrow N & \searrow \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$	CH ₂) 4 (NNO ₂) 4	296.8		276	expl.	insol.		•			
	1,3,5-Trinitrobenzene (TNB; benzite)		C ₆ H ₃ (NO ₂) ₃	213.1	1.69	121	312	.030 ¹⁵ insol.	1.9 ¹⁸ sol.	1.5 ¹⁸ in ether 59 ¹⁷ in acetone	2.2×10 ⁻⁴ mm 820°C	520 (3)	Токіс
	4-hydroxyazobenzene (Benzeneazophenol)	H: N () OH	C ₁₂ H ₁₀ N ₂ O	198.2		156	225 insalightly decomposes	insol. / ses	v.sol.	V.sol in ether Sol. in benzene			

^{*}from Battelle estimates +for $K_{OC}\colon$ (in mm solution/gm organic content)

⁽¹⁾ Spanggord, 1980. (2) Spanngord, 1978 (extrapolated by Battelle). (3) Estimated by Battelle.

TABLE A-2. PHYSICAL PROPERTIES OF METALS AND METALLIC COMPOUNDS

	Compound	Molecular Weight	Specific Gravity	Melting Point (^O C)	Boiling Point (^O C)	Cold Water Solubility	Hot Water Solubility	Other Solvents	Toxicity
	Cadmium (Cd)	112.4	8.6520	321	. 766	Insoluble	Insoluble	Sol. in acid, NH ₄ NO ₃	Toxic
	Chromium (Cr)	,52.0	7.10 ²⁰	1865	2670	Insoluble	Insoluble	Sol. in $H_2^{SO_4}$, HCl in HNO ₃	Skin and mucous irritant
Į	Copper (Cu)	63.6	8.9220	1083	2580	Insoluble	Insoluble	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Toxic
4-2	(Pb)	207.2	11.34 ¹⁶	327.5	1730	Insoluble	Insoluble	Sol. in HNO3, hot H ₂ SO ₄ insol. in HC1, cold H ₂ SO ₄	Cumulative poison; carcinogen
	Zinc (Zn)	65.4	7.14 ²⁰	419.5	906	Insoluble	Insoluble	Sol, in acid, alkali, acetic acid	Only toxic in zinc oxide form
	Lead Az ide PbN ₆	291.3	.8-1.8		350 explodes	.023 ¹⁸ (gm/100cc)	.09 ⁷⁰ (gm/100cc)	Sol. in acetic acid Insol. in NH4OH	
	Lead Styphnate (2,4,6- Trinitroresorcinate) O ₂ N	230.0 e) Pb	1.0-1.6		•	.04 ²⁰ (gm/100cc)		Sol. in NaOH,	

TABLE A-3. PHYSICAL PROPERTIES OF SOLVENTS

	ous effect on-		nic; in ns	cous high tions	nic: high tions			
Toxicity	Nutagenic. Eye f mucous irritant; naroctic effect of high con-	Poisonous	Carcinogenic; narcotic in high con- centrations	Skin & mucous irritant; toxic in high concentrations	Carcinogenics toxic in high concentrations			Poisonous
Vapor Pressure	100 mm 620°C	100 mm #32°C	100 mm at 10.4oc	442 mm 620°C	6.85x10 ⁻⁷ mn #20°C	.01 mm #20°C	1 . 2mm 2200 ^O C	1.5×10 ⁻⁷
Normalized Sorption Partition Coeff.,	2.48	28				₽99	11,300	
s) Ether	Sol.	Misc.	Misc.	sol.	sol.	gol.		v.Sol.
Solubility (in 100 parts) Water Alcohol Ether	sol.	Misc.	Misc.	sol.	sol.	Sol.		gol.
Solub (in) Water A	Insol.	Insol.	.82 20	81.80l.	Insol.	Insol.		Insol.
Boiling Point (^O C)	74.1	67.1	61.3	34.6	007	ca 375	230° at Smm	185
Melting Point (OC)	-30.4	-73	-63.5	-116.2	156	ııı	005-	109
Specific Gravity	1.354	1.4720	1.48	.714	1.27	1.254	20 . 986 ₂₀	
ar Pormula	с1 3ссн3	ст2сссти	сист	C2H5OC2H5	C16H10	C ₁₆ H ₁₀	C 24 ^H 38 04	C14H9C15
Molecular Weight	133.4	131.4	119.4	14.1	202.2	202.2	390.5	354.5
Structure	H 10 1 - 1 - 10 1 - 1 - 10	C1, C1	C1 - C - H	H H L C C C C C L S H H H H H H H H H			C00CH2CH (C2H5) (CH2) 3 CH3 C00CH2CH (C2H5) (CH2) 3 CH3	$c_1 - \left\langle \begin{array}{c} cc1_3 \\ -c_1 \\ -c_1 \\ +c_1 \\ +c_1 \\ +c_1 \\ +c_1 \\ +c_2 \\ +c_2 \\ -c_1 \\ +c_2 \\ +c_3 \\ -c_4 \\ +c_4 \\ +c_4 \\ +c_5 \\ +c_5 \\ +c_6 \\$
. Compound	1,1,1-trichloroethane (methylchloroform) chlorothene)	Trichlorouthylene (ethylene trichloride; ethinyl trichloride)	Chloroform (trichloromethane)	Diethyl ether (ether, ethyl ether, ethoxyethane)	Pyrene (Henzold,e,f) phenanthrene)	Fluoranthene (1,2-benzacenaphthene)	Bis (2-ethylhexyl) phthalate (octoil;dioctoyl phthenlate)	Dichloro-diphenyl- Trichloroethane (DDT)

APPENDIX B SAMPLE BALLOTS FOR TECHNOLOGY ASSESSMENT



APPENDIX B

SAMPLE BALLOTS FOR TECHNOLOGY ASSESSMENT

The form used for the first-level technology assessment is shown on Figure B-1. Each participant was given 10 separate ballots, one for each criterion in the first-level assessment. The 52 technologies were listed on each ballot, and were rated +, 0, or - for the criterion on that page. Ample room was allowed for the explanations and comments of the participants.

A different ballot format was used for the second-level evaluation, which dealt with a more manageable number of technologies. As shown on Figure B-2, each technology was on a separate page. The seven criteria were listed on the ballot, and the processes were again rated +, 0, or - in each category.

TECHNOLOGY ASSESSMENT FORM

		Ι.		<u> </u>	
	Technology	+	0		Comments
Chem	ical				
1. 8	Sulfur-based reduction				
2. 1	Enercol oxidation process			n.	
3. 5	Solvent extraction				
	Chemical reduction with sodium boro- nydride				
5. !	Free radical oxidation				
	Decontamination of soils with Franklin solvent				
7. (Carbon adsorption				
8. 1	Ion exchange				
9. 8	Surfactant complexing				
	Solvent extraction (Acurex process)				
11. V	% ashout				
	Removal of metals using dithiocarbo- nate				
	Philadelphia Quartz (PQ) process for removing heavy metals				
14. 1	Removal of heavy metals using cellu- Lose xanthalate				
15. I	Penton's reagent				
16. E	Base-initiated reactions				

Figure B-1. First-level technology assessment form.

TECHNOLOGY ASSESSMENT FORM

Technology	+	0	-	Comments
Biological				
1. Microbial bioaccumulation of m	etals			
2. Immobilized cells				
3. Vermicomposting				
4. Composting				
5. Aerobic biodegradation	·			
6. Biodegradation using adapte microbed	đ			
7. Anaerobic biodegradation			<u> </u>	
8. Vegetative uptake				
9. Landfarming				
10. Bioreclamation of soils (GDS process)				
11. Fluidized bed biological				
12. Anaerobic/aerobic cycling				1

Figure B-1. (Continued)

TECHNOLOGY ASSESSMENT FORM

Technology	+	0	-	Comments
Thermal				
1. Vertical well chemical reactor				
2. Multiple hearth incinerator				
3. Rotary kiln incinerator				
4. Molten salt incinerator				
5. Wet air oxidation				
6. In-situ vitrification				
7. Plasma arc pyrolysis				
8. Microwave plasma				
9. Burning/torching	·	<u> </u>		
10. Hot air/steam stripping				
11. Low temperature thermal				
12. Supercritical water oxidation				
13. Fluidized bed incineration			<u> </u>	
14. High temperature fluid wall			<u> </u>	
15. In-situ microwave				
16. Laser-initiated thermal decomposition				

Figure B-1. (Continued)

TROUDINGS ASSESSMENT FORM

Technology	+	0	-	Comments
Physical				
1. Secure landfill				
2. Slurry wall				
3. Grouting				
4. Sea bed disposal				
5. Encapsulation				
- Microencapsulation - Macroencapsulation				
6. Fixation				
7. Stabilization (chemical admixing)				
8. Magnetic separation				

Figure B-1. (Continued)

SECOND-LEVEL EVALUATION

	Technology	+	0	-	Comments
ri	eria				
rimo	to commercialization				
eroj	orietary status				
38 t	imated relative commercialization cost				
sst.	imated relative operational costs				
Sn v	ironmental impact				
Jni	t process interactions				
Ver	satility				
Con	siderations	<u>Yes</u>	<u>No</u>		Comments
1.	Is there process equipment, hardware, software, or a demonstration system currently available for field demonstration or pilot-scale testing?				
2.	Can reliability be designed into the hard- ware/software subsystems without exorbi- tant expense?				
3.	Are exotic or strategic materials required?				
4.	Are there materials-handling risks to be assessed?				

Figure B-2. Second-level technology assessment form.

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